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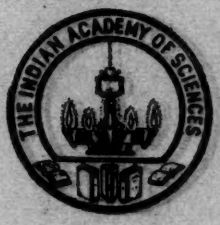

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HUYGHENS' PRINCIPLE AND THE DIFFRACTION OF LIGHT

Part I. Theoretical Considerations

By Sir C. V. Raman

(*Memoir No.* 118 *from the Raman Research Institute, Bangalore-6*)

Received July 23, 1959

1. Introduction

The first three chapters of Huyghens' Treatise on Light published in the year 1690 carry the titles "On Rays Propagated in Straight Lines"; "On Reflection"; "On Refraction". They seek to explain the familiar facts of geometrical optics on the basis of the idea that light consists of waves propagated outwards from the original source in the luminiferous medium. Huyghens based himself on certain hypotheses regarding the nature of the medium and on the nature of the light waves themselves. The adequacy of his explanations of the rectilinear propagation of light and of the geometric laws of reflection and refraction of light has necessarily to be viewed against the background of those hypotheses. The treatise of Huyghens exerted a great influence on the development of the wave-theory of light in later years. Surprisingly enough, however, his ideas were not correctly understood by those who followed him. They ascribed to Huyghens various statements not to be found in his treatise and then proceeded to criticise his ideas in an unjustifiable manner. In a recent memoir by the present author published in these *Proceedings*, a precis was given of the first three chapters of Huyghens' treatise and it was shown that, if we accept the hypotheses of Huyghens regarding the nature of the luminiferous medium and the nature of light, the rest of his argument forms a coherent and complete explanation of the facts which he sought to elucidate.

Treatises on physical optics devote a good deal of space to an exposition of what they refer to as "Huyghens' Principle" and the more advanced treatises proceed to sketch a mathematical development which is described as "The Rigorous Formulation of Huyghens' Principle" and associate it with the name of Kirchhoff. The readers of those treatises are invited to believe that Huyghens' Principle as thus formulated is an adequate basis for

the explanation of the phenomena of the diffraction of light. However, in the author's memoir mentioned above, it was indicated that the explanations referred to are vitiated by the misunderstanding of the ideas of Huyghens on which they claim to be based. It is the object of the present memoir to go more fully into these matters and to show that the concepts of Huyghens can indeed be used as a framework for an elementary theory of diffraction, but that they lead to results which are wholly different from those indicated by the well-known formulæ of Kirchhoff. Extensive experimental studies of the phenomena of the diffraction of light have also been carried out by the author and the results of the same are reported in the second part of this memoir. They vindicate the present theoretical approach and contradict the consequences of Kirchhoff's theory, showing thereby that the latter is unsustainable.

2. THE WAVE-OPTICS OF HUYGHENS

When we examine the first three chapters of Huyghens' treatise, it becomes clear that a certain basic idea regarding the propagation of light underlies them all. What Huyghens sought to show in his first chapter is that in a homogeneous medium, each little piece of the primary wave emerging from a source of light is capable of travelling in a direction normal to itself more or less independently and that the primary wave-front is the locus or surface at which all the little pieces of which it is made up arrive at the same instant. The explanation of the laws of reflection and of refraction given in the second and third chapters proceeds on the same basis. Each piece of the original wave-front from the light-source on reaching the boundary between two media of which the optical properties are different finds itself unable to continue on its original course by reason of that fact. Such a situation arises, for example, if both media admit of the propagation of light through them but with different velocities. In these circumstances, the individual pieces of the wave take fresh paths which are different in the two media; the directions of travel in each case are such that the pieces of the original wave-front which are diverted from their path on reaching the boundary join up together again and form new wave-fronts in each medium. A simple geometric construction enabled Huyghens to ascertain the directions of travel which enable these conditions to be satisfied in each medium, from which again the geometric laws of reflection and refraction follow immediately. Huyghens' derivation of these laws is both simple and convincing. Regarded as a physical theory, it is also highly successful since it demonstrates that the refractive indices of the two media are in the inverse ratio of the velocities of light in them.

The concept of " partial waves " introduced by Huyghens plays a most important role in his arguments and indeed forms the hard core of his theory. It is not introduced *ad hoc* but is put forward with a definite physical justification wherever it is brought in and made use of. In the first chapter of the treatise in which the rectilinear propagation of light is sought to be explained, the partial waves considered are those which arise by reason of the structure which the luminiferous medium is assumed to possess. Each individual particle of the medium when disturbed by the passage of the primary wave becomes a source from which partial waves spread out in all directions, but these partial waves by reason of their excessive feebleness can produce a sensible effect only when a great number of them arrive simultaneously at a given point of observation: this again is only possible when the sources of the partial waves all lie on the straight line joining the original source and the point of observation. Accordingly, it is justifiable to regard the primary wave as having travelled out along that line and identify it with the summation of the partial waves of which the effects are superposed at the point of observation.

The partial waves considered in the second and third chapters of the treatise have a different origin. Here, Huyghens found himself compelled to introduce the idea that the elementary *areas* of the surface of separation between two media having different optical properties become sources of partial waves: the waves which go back into the first medium build up the reflected wave-front, while those which go forward into the second medium build the refracted wave-front.

3. The Nature of Diffraction Phenomena

When we speak of the diffraction of light, we have in mind certain effects which are observed when the free propagation of light is modified or influenced by the presence of obstacles in its path. It is clear that the nature of the obstacles, including their optical properties and their configuration in space, would determine these effects and it follows that the factors referred to would play the leading role in any theory of diffraction. If, bearing this in mind, we seek to discover in the ideas of Huyghens a possible approach towards an understanding of the phenomena of diffraction, it becomes apparent that no such approach can be found in his explanation of the rectilinear propagation of light. On the other hand, his theory of reflection and refraction does offer itself as a basis. For, as already stated, it makes use of the idea that each element of area of the boundary between two media on which light is incident is a source of partial or secondary waves in the two media. Conceptually, these waves can diverge from each element

in various directions, but the requirement imposed by the theory of Huyghens that the disturbances originating at the different elements of area should arrive simultaneously at a common wave-front fixes the actual direction of their movement. If, instead of considering light waves as simple pulses, we take account of their periodic nature and of the possibility of interferences between the secondary or partial waves having their origin at the different elements of area on the boundary between the two media, the restriction of the observable effect to precisely defined directions ceases to exist. In other words, the diffraction of light becomes a possibility.

Thus, we arrive at the important conclusion that a theory of diffraction which makes use of Huyghens' concept of partial waves has to base itself on the waves of that nature which arise in association with the reflection and refraction of light at the boundary between two media with different optical properties.

4. THE CHARACTER OF THE SECONDARY WAVES

Accordingly, we proceed to consider the partial or secondary waves having their origin at the elements of area of a boundary between two media of different refractive indices on which light is incident. There would clearly be two sets of such secondary waves travelling out respectively into the two media. The velocity of travel and the amplitude of the disturbance in the two sets being different, they must be considered as completely distinct from each other. If both media are isotropic, the configuration of the secondary waves in each medium would be hemispheres. The particular circumstances of the case, *viz.*, the refractive indices of the two media, the angle of incidence of the primary waves on the boundary and the state of polarisation of the incident light would determine the manner in which the energy of the incident radiation would be divided up between the reflected and refracted wave trains. The same circumstances would also determine the amplitude of the disturbance in the secondary waves sent out respectively into the two media.

The theory of diffraction proceeds by considering the secondary radiations emitted in different directions by the elements of area of the reflecting or refracting boundary and summing up their effects at the point of observation, having regard to their amplitudes and phases at that point. The first step in the theory is to write down a formal expression for the partial or secondary waves. Their amplitude would clearly be proportional to the amplitude of the primary disturbance incident on the boundary and reflected or refracted by it, as the case may be, and hence we have to find a dimensionless magnitude which expresses the proportionality. The quantities which might appear in it include, firstly, the element of area dS on the boundary,

r the radius vector joining the element with the point of observation, ϕ the angle between r and the normal to the plane of the boundary, and λ the wave-length of the light. It is reasonable to assume that the solid angle subtended by the element of area $d\mathbf{S}$ at the point of observation would determine its effect at that point. This solid angle is $d\mathbf{S}\cdot\cos\phi/r^2$. If we multiply this by the quantity r/λ, we obtain the dimensionless number $d\mathbf{S}\cos\phi/\lambda r$, which exhibits an inverse proportionality both to r and to λ; the inverse proportionality with respect to r is to be expected for waves diverging outwards hemispherically, while the inverse proportionality with respect to λ is an indication that we are dealing with a wave-optical effect.

The important result emerging from the above is the appearance of $\cos\phi$ in the expression for the amplitude of the secondary waves. We shall refer to it as the *obliquity factor*. It has the value unity in the direction of the normal to the reflecting or refracting boundary, while it vanishes in any direction which lies in the plane of that boundary. It is evident that if we are concerned with a reflecting or refracting boundary of finite area and if the point of observation is at a sufficiently great distance from it, the angle ϕ may, without sensible error, be assumed to be the same for all the elements of area. It is evident also that in such a case, when we proceed to investigate the nature of the diffraction pattern at such distant point by summing up the effects of the elements of area with due regard to their phases and squaring the resultant amplitude to obtain the observed intensity, the square of the cosine of the obliquity, *viz.*, $\cos^2\phi$ would appear in it as a multiplying factor.

The result stated above is obviously of very general validity in respect of the diffraction patterns of the Fraunhofer class observed in various circumstances. All that is required is that the diffraction arises by reason of the limitation of the area of a plane surface at which light is reflected or through which it is transmitted; in the case of reflection, the material may be either a dielectric or a metal. It is not necessary that the surface should be continuous or that it should have uniform reflecting or transmitting power over the entire area. It might, for example, consist of several parallel strips, thus forming a plane diffraction grating. Further, since refraction at the boundary between two media which differ only infinitesimally in refractive index is equivalent to a simple transmission, it follows that the result would also be applicable to diffraction patterns of the Fraunhofer class arising from the passage of light through apertures in thin opaque screens.

5. Verification of the Obliquity Law

Any elementary treatment of diffraction theory can only be expected to be valid when the linear dimensions of the diffracting aperture are large

compared with the wave-length of the light. As the angular spread of the diffraction pattern would in these circumstances be small, an experimental test of the law of the secondary wave might seem impracticable. Fortunately, however, this is not the case. For, the angle of diffraction ϕ is measured from the direction of the normal to the aperture and hence when the incidence of the light on the aperture is oblique, ϕ may be large enough for the factor $\cos^2\phi$ to vary rapidly over the area of the diffraction pattern. Further, at such settings the diffraction patterns are spread out over a fairly wide angular range even when the dimensions of the aperture are many times larger than the wave-length. In these circumstances, the effect of the $\cos^2\phi$ factor on the distribution of the intensity in the pattern becomes conspicuous and can indeed easily be observed and measured.

We may illustrate these remarks by considering a simple case, *viz.*, a diffracting aperture which is a plane strip bounded by parallel straight edges. As is well known, when the effects due to the infinitesimal elements of such an aperture are summed up, the expression obtained for the intensity in its Fraunhofer pattern includes a factor of the form $\sin^2\zeta/\zeta^2$. This factor has a maximum value when $\zeta = 0$, and vanishes when $\zeta = \pm\pi$, $\pm 2\pi$, $\pm 3\pi$, etc. Since the value of $\sin^2\zeta/\zeta^2$ is unaltered by a reversal of the sign of ζ, the graph of the function when set out with ζ as the abscissa is a symmetric curve in which the maxima on either side intermediate between the zero values are of equal intensity. The factor $\cos^2\phi$ by which the expression for the intensity is multiplied would, however, modify this situation to an extent determined by the circumstances of the case.

In the particular case of normal incidence of the light on the aperture, $\zeta = \pi a \sin\phi/\lambda$, a being the width of the aperture, λ the wave-length and ϕ the angle of diffraction as already defined. More generally, when the light is incident on the aperture at an angle θ in a plane normal to its edges, $\zeta = \pi a(\sin\phi - \sin\theta)/\lambda$. Differentiating this, we obtain $d\zeta = \pi a/\lambda . \cos\phi\, d\phi$. Hence, as the incidence is made more oblique and $\cos\phi$ diminishes in value, the angular spread of the pattern determined by the increments of $d\phi$ becomes greater. The bands for which ϕ is greater than θ would also appear more widely spaced than those for which ϕ is less than θ. In these circumstances, the multiplying factor $\cos^2\phi$ would have a very conspicuous influence on the distribution of intensity in the pattern. The bands for which ϕ is greater than θ would be much less intense than those for which ϕ is less than θ; indeed as ϕ approaches the limiting value $\pi/2$, the intensity in the former cases would become vanishingly small.

6. The Results of Experimental Study

The present theory of diffraction and that of Kirchhoff thus differ fundamentally in the observable results which they indicate. This is scarcely a matter for surprise since they approach the diffraction problem from completely different points of view. Whereas the diffracting body plays the leading role in the present theory, it is not considered at all in the Kirchhoff formulation; the latter is based on the idea that the primary radiation from a source situated in free space can be expressed as a summation of secondary radiations from a set of sources distributed over a closed surface in free space enclosing the point of observation. The present theory leads to the result that the amplitude of the secondary waves vanishes along the plane of the surface at which they originate and increases progressively as we move away from that plane towards the direction of its normal. On the other hand, the Kirchhoff formulation indicates that the secondary waves have a maximum amplitude in the forward direction of the light rays from the original source and zero amplitude in the backward direction. The difference between the consequences of the two theories is of such a striking character that it is a simple matter by means of experimental study to decide between them.

In view of the importance of the issue here raised for a correct understanding of the theory of the diffraction of light, numerous experimental studies have been carried out by the writer. Diffracting apertures of various sizes ranging from several centimetres down to fractions of a millimetre have been employed. The angles of incidence of the light on the apertures have been varied from normal incidence up to grazing incidence. The circumstances in which the diffraction manifests itself have also been varied to include various cases, *e.g.*, the reflection of light at a plane surface of a dielectric or metal, the emergence of light after refraction through a transparent medium at various angles, the internal reflection of light within a transparent medium at various incidences and the transmission of light through apertures in thin opaque screens. The cases investigated include both simple and multiple apertures and plane diffraction gratings prepared by various techniques and operating by reflection as also by transmission. In all the cases investigated, the consequences of the present theoretical approach are completely vindicated by the facts of observation.

7. Summary

The conventional treatment of diffraction problems based on the so-called Principle of Huyghens as analytically formulated by Kirchhoff is based on a misunderstanding of the original ideas of Huyghens regarding the propagation of light. It seeks to express the luminous effect due to the primary

source as a summation of the effects of secondary sources situated on the elementary areas of a surface in free space enclosing the point of observation. Since the diffraction of light is a consequence of the presence of obstacles in the path of the light waves, the optical character of the obstacles and their configuration in space are of the very essence of the problem. It follows that the approach adopted in the Kirchhoff theory is misconceived and erroneous. It is however possible to base a theory of diffraction on Huyghens' concept of partial waves and his explanation of the reflection and refraction of light at the boundary between media with different optical properties. But this leads to results which differ fundamentally from those indicated by Kirchhoff's formula. It is shown that the issue which thus presents itself is readily capable of experimental test.

A NOTE ON THE INTERACTION BETWEEN NUCLEON AND ANTI-NUCLEON

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Abstract

The interaction potential between nucleon and anti-nucleon is derived by using the new Tamm-Dancoff formalism.

Introduction

With the discovery of anti-nucleons ($\bar{N}$), many experiments on nucleon (N)—anti-nucleon ($\bar{N}$) scattering have been performed in the energy range 100–400 Mev. In order to interpret the results of these experiments, we must know the forces between N and $\bar{N}$. The interaction potential between N and $\bar{N}$ has been recently studied by Chew and Ball (1958). As Chew (1959) pointed out, if we correctly understand charge conjugation, we can expect the interaction potential to have the general features of N-$\bar{N}$ potential as given by Gartenhaus (1955) except that the N-N potential will have opposite sign to that of N-N. In this note we have derived an expression for N-$\bar{N}$ potential due to an exchange of single pion using the new Tamm-Dancoff formalism of Dyson (1953).

As is well known in Dyson's new Tamm-Dancoff formalism, we employ the true or physical vacuum ψ_0 instead of the bare vacuum and the vacuum self-energy is thereby eliminated. Denoting by $A(\vec{p}, \vec{q})$ the amplitude for finding a nucleon of momentum $\vec{p}$ and anti-nucleon of momentum $\vec{q}$ in the state ψ, *i.e.*,

$$A(\vec{p}, \vec{q}) = [\psi_0, b(\vec{p})\, d(\vec{q})\, \psi]$$

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we obtain

$$(E_{p,\,q} - \epsilon)\, A(\vec{p}, \vec{q}) = \{\psi_0, [H_1, b(\vec{p})\, d(\vec{q})]\, \psi\} \tag{1}$$

where $E_{p,q}$ is the kinetic energy of free N and $\bar{N}$, ϵ is the total energy of the system and $b(\vec{p})$ and $d(\vec{q})$ are the annihilation operators for N and $\bar{N}$ with momentum $\vec{p}$ and $\vec{q}$ respectively. H_I is the Yukawa Hamiltonian in Schrodinger representation given by

$$H_I = g \int \bar{\psi}(\vec{x})\, \gamma_5\, \tau_i\, \psi(\vec{x})\, \phi_i(\vec{x})\, d^3x. \tag{2}$$

On evaluating the commutator on the right-hand side of (1), we find that the amplitude $A(\vec{p}, \vec{q})$ will be connected to various other amplitudes. But in order to obtain an integral equation for $A(\vec{p}, \vec{q})$ we will retain only those intermediate amplitudes which can be related back to $A(\vec{p}, \vec{q})$. Thus we consider only the following amplitudes $A(\vec{k}, \vec{q}, \vec{p} - \vec{k};)$, $A(\vec{k}, \vec{q};\ \vec{k} - \vec{p})$, $A(\vec{p} + \vec{q};)$, $A(; -\vec{p} - \vec{q})$, $A(\vec{p}, \vec{k}, \vec{q}, -\vec{k};)$ and $A(\vec{p}, \vec{k};\ \vec{k} - \vec{q})$ where the momentum occurring before the semicolon refer to Dyson's *plus* particles and the momentum occurring after the semicolon refer to Dyson's *minus* particles. The first two and the last two amplitudes stand for a $N\bar{N}$ and a meson while the middle two amplitudes refer to a meson alone.

In the centre of mass system of $N\bar{N}$ we have $\vec{p} = -\vec{q}$. Denoting by $A(\vec{p})$, the amplitude $A(\vec{p}, -\vec{p})$ the integral equation for $A(\vec{p})$ is given by

$$\begin{aligned}
&[2E(p) - \epsilon]\, A(\vec{p}) \\
&\quad = \frac{g^2}{(2\pi)^9} \frac{m}{E(p)} \Big[\bar{u}(\vec{p}) \int d^3k\, \frac{m}{E(k)} \frac{1}{2\omega(p-k)} \\
&\qquad \times \frac{\gamma_5 \tau_i u(\vec{k})\, \bar{u}(\vec{k})\, \gamma_5 \tau_i}{E(k) + E(p) \pm \omega(p-k) - \epsilon}\, u(\vec{p})\, A(\vec{p}) \\
&\qquad - \bar{u}(\vec{p}) \int d^3k\, \frac{m}{E(k)} \frac{1}{2\omega(p-k)} \\
&\qquad \times \frac{\gamma_5 \tau_i u(\vec{k})\, \bar{v}(-\vec{k})\, \gamma_5 \tau_i\, v(-\vec{p})}{E(k) + E(p) \pm \omega(p-k) - \epsilon}\, A(\vec{k})
\end{aligned}$$

$$+\frac{1}{2\mu}\bar{u}(p)\int d^3k\,\frac{m}{\mathrm{E}(k)}\frac{\gamma_5\tau_i\bar{v}(\vec{k})\,\gamma_5\tau_i u(-\vec{k})\,v(\vec{p})}{\pm\mu-\epsilon}\,\mathrm{A}(\vec{k})$$

$$-\int d^3k\,\frac{m}{\mathrm{E}(k)}\,\frac{1}{2\omega(p+k)}$$

$$\times\frac{\bar{v}(\vec{k})\,\gamma_5\tau_i\bar{u}(\vec{p})\,\gamma_5\tau_i u(-\vec{k})\,v(-\vec{p})}{\mathrm{E}(p)+\mathrm{E}(k)\pm\omega(p+k)-\epsilon}\,\mathrm{A}(\vec{k})$$

$$+\int d^3k\,\frac{m}{\mathrm{E}(k)}\,\frac{1}{2\omega(p+k)}$$

$$\times\frac{\bar{v}(\vec{k})\,\gamma_5\tau_i\bar{v}(\vec{p})\,\gamma_5\tau_i v(\vec{k})\,v(\vec{p})}{\mathrm{E}(p)+\mathrm{E}(k)\pm\omega(p+k)-\epsilon}\,\mathrm{A}(\vec{p})\Big] \qquad (3)^*$$

We now neglect the nucleon recoil energies $\mathrm{E}(p)$ and $\mathrm{E}(k)$ when they occur together with meson energy ω. Also we omit the terms having $-\omega$ in the energy denominator. The first and last terms in (3) represent self-energy terms and thus they will be omitted. In these circumstances we can approximate Dirac spinors by their large components. Thus the 'potential' $\mathrm{V}(\vec{k})$ in the momentum space is identified to be

$$\mathrm{V}(\vec{k})=-\frac{g^2}{(2\pi)^3}\vec{\tau}_1\cdot\vec{\tau}_2\frac{(\vec{\sigma}_1\cdot\vec{k})(\vec{\sigma}_2\cdot\vec{k})}{[\omega(k)]^2}+\frac{g^2}{(2\pi)^3}\vec{\tau}_1\cdot\vec{\tau}_2\frac{1}{2\mu^2} \qquad (4)$$

The potential in configuration space will be given by, if γ denotes the relative distance,

$$\mathrm{V}(\gamma)=-\frac{g^2}{(2\pi)^3}\vec{\tau}_1\cdot\vec{\tau}_2\left\{\frac{\vec{\sigma}_1\cdot\vec{\sigma}_2}{\gamma}\int_1^\infty\frac{kdk}{[\omega(k)]^2}\sin k\gamma+3\mathrm{S}_{12}\int_0^\infty\frac{kdk}{[\omega(k)]^2}\right.$$

$$\left.\times\left[\left(\frac{k^2}{3\gamma}-\frac{1}{\gamma^3}\right)\sin k\gamma+\frac{k}{\gamma^2}\cos k\gamma\right]\right\}$$

$$+\frac{g^2}{(2\pi)^3}\frac{\vec{\tau}_1\cdot\vec{\tau}_2}{2\mu^2}\delta(\gamma) \qquad (5)$$

---

* Here we have used the notation + and − in the denominator to indicate the sum of two terms in the integrand one involving a denominator with + before ω and another having denominator with − before ω. This is done purely for convenience in printing to avoid unnecessary duplication of terms.

where S_{12} is the familiar 'tensor force' operator, *i.e.*, $S_{12} = 3(\vec{\sigma}_1 \cdot \gamma)(\vec{\sigma}_2 \cdot \gamma)/\gamma^2$. An almost similar potential given below was obtained by Tarasov (1956) using old Tamm-Dancoff formalism

$$V(\gamma) = -\tfrac{1}{3}\vec{\tau}_1 \cdot \vec{\tau}_2 \frac{g^2}{4\pi}\left(\frac{\mu}{2m}\right)^2 \vec{\sigma}_1 \cdot \vec{\sigma}_2 + S_{12}\left[1 + \frac{3}{\mu\gamma} + \frac{3}{\mu\gamma^2}\right]\frac{e^{-\mu\gamma}}{\gamma}$$

$$-\tfrac{1}{3}(\vec{\sigma}_1 \cdot \vec{\sigma}_2)(\vec{\tau}_1 \cdot \vec{\tau}_2)(2m)^{-2}\,\delta(\gamma)$$

$$+\frac{(\vec{\tau}_1 \cdot \vec{\tau}_2 + 3)(\vec{\sigma}_1 \cdot \vec{\sigma}_2 - 1)}{4\mu(2m - \mu)}\,\delta(\gamma) \qquad (6)$$

The first term in (5) should adequately describe the potential when V is of the order of Compton wavelength of pion. The second term denotes a 'contact' potential but as is well known we should not rely on it under the approximations made here. The first term agrees with that of Garterhaus potential for a single pion exchange except for the sign provided we replace g by the renormalised coupling constant. Of course, we are aware of the fact that in a Tamm-Dancoff formalism such as the one which we have employed in this note, renormalisation is not a consistent procedure.

In conclusion, we wish to thank Messrs. R. Vasudevan and K. Venkatesan for interesting discussions.

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THEORY OF THE ANOMALOUS DISPERSION METHOD OF DETERMINING THE STRUCTURE AND ABSOLUTE CONFIGURATION OF NON-CENTROSYMMETRIC CRYSTALS

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1. Introduction

This paper deals with the theory of a method of determining simultaneously both the structure and absolute configuration of a non-centrosymmetric crystal. The method is based on the well-known effect of anomalous dispersion, namely, the fact that the scattering power of an atom depends on the frequency of the incident X-radiation, particularly in the vicinity of the absorption edge of the atom. The method was evolved in the course of the analysis of the structure of the monohydrochloride dihydrate of the amino-acid L(+) lysine. The determination of the structure of this non-centric crystal by classical methods was rather difficult because of the non-availability of the hydrobromide derivative and also because of the large repeat period of the monoclinic axis (13·31 A), which corresponds to the only available centrosymmetric projection. However, by making use of the presence of chlorine, which was found to be a sufficiently strong anomalous scatterer even for the usual CuK_α-radiation, the structure could be solved.

The method is based on the possibility of phase determination from a straightforward experimental measurement of the intensity-differences $\Delta|F|^2$ between pairs of inverse reflections hkl and $\bar{h}\bar{k}\bar{l}$ produced by the imaginary component $\Delta f''$ of the scattering factor. Tnis imaginary component comes into play only on the short wavelength side of the absorption edge and does not exist on the long wavelength side. There is, however, a small depression $\Delta f'$ of the real part of the scattering power on either side of the absorption edge. In general, either $\Delta f'$ or $\Delta f''$ can be made use of for the purpose of phase determination or both can be used. The use of either one by itself leads only to an ambiguous solution of the phase problem, but the simultaneous use of both leads to a unique solution.

The actual method employed in the case of lysine only made use of $\Delta f''$ and therefore this required only intensity measurements made at a single wavelength. However, it is a special case of a more general method which involves measurements at two wavelengths. For this reason, a coherent picture of the whole theory will be presented in this paper, though more emphasis will be laid on the single wavelength imaginary component method. Only the latter method has so far been experimentally tested. The method has been shown to work in the case of the hydrochloride of the amino-alkaloid L (+) ephedrine (Ramachandran and Raman, 1956; Raman, 1958). The latter is a crystal whose structure has been already solved by classical methods (Phillips, 1954). It was chosen for analysis because it was desirable that the anomalous dispersion method must be tried, first of all, in the case of a crystal of known structure. The results were quite encouraging and therefore the method was applied to the case of the monohydrochloride dihydrate of L (+) lysine, a crystal whose structure was completely unknown to start with. The structure of this non-centric crystal could be solved by the anomalous dispersion method, without recourse to auxiliary techniques and without making use of a centro-symmetric projection. The results of this investigation are being published elsewhere (Raman, 1959) and the present paper is only concerned with the theoretical possibilities of exploiting the anomalous dispersion effect towards a solution of the phase problem, with particular reference to non-centric crystals. Some aspects of the theory have been given by other workers, for instance, Okaya and Pepinsky (1956), Mitchell (1957) and Peerdeman and Bijvoet (1956). In all the cases, the work has been stimulated by the pioneering researches of Bijvoet who, for the first time in 1951, determined the absolute configuration of optical antipodes from a study of the intensity differences $\Delta \mid F \mid^2$ between pairs of inverse reflections hkl and $\bar{h}\bar{k}\bar{l}$. For this reason, the intensity differences between inverse reflections will be called the Bijvoet inequality.

2. Theory of the Two Wavelength Anomalous Dispersion Method

We will now outline the theory of the generalised anomalous dispersion method of determining the structure of crystals. The method is applicable both to non-centric as well as to centro-symmetric crystals. It can be adopted provided the unit cell of the crystal contains at least one atom, or a group of P-crystallographically equivalent atoms, for which the components $\Delta f_P'$ and $\Delta f_P''$ of the atomic scattering factors f_P are significant while for the remaining (N − P) atoms these components are negligible. A unique determination of the phase angles of the complex structure factors

is possible provided the intensities are measured at two wavelengths, the first wavelength being chosen to be slightly shorter than the absorption limit λ_P of the P-atoms, so that both $\Delta f_P'$ and $\Delta f_P''$ are significant and the second wavelength being chosen far away from λ_P so that both the components are negligible.

It is then obvious that the scattering factors of one of the P-anomalous scatterers denoted by the suffix P_j at the first wavelength will be given by

$$f_{Pj} = f_{Pj}^0 + \Delta f_{Pj}' + i\Delta f_{Pj}'' \tag{1}$$

and at the second wavelength it will just be equal to f_{Pj}^0. The scattering factors of the Q non-anomalous scatterers denoted by Qk will be given by f_{Qk}^0 at both the wavelengths (where $Q = N - P$). Let F_N denote the structure factor of any particular reflection at the first wavelength and F_N° the structure factor of the same reflection at the second wavelength. Denote the structure factors of the inverse reflection $\bar{h}\bar{k}\bar{l}$ by a bar over the corresponding symbol for the reflection hkl and the complex conjugate of any particular structure factor by a star.

It is then obvious that the structure factor F_N will be given by

$$F_N = F_Q^0 + F_P^0 + F_P' + F_P'' \tag{3}$$

where

$$F_Q^0 = \sum_k f_{Qk}^0 \exp. 2\pi i (hx_{Qk} + ky_{Qk} + lz_{Qk}) \tag{4}$$

$$\begin{aligned} F_P^0 &= \sum_j f_{Pj}^0 \exp. 2\pi i (hx_{Pj} + ky_{Pj} + lz_{Pj}) \\ &= |F_P^0| \exp. i\alpha_P^0 \end{aligned} \tag{5}$$

$$\begin{aligned} F_P' &= \sum_j \Delta f_{Pj}' \exp. 2\pi i (hx_{Pj} + ky_{Pj} + lz_{Pj}) \\ &= |F_P'| \exp. i\alpha_P' \end{aligned} \tag{6}$$

$$\begin{aligned} F_P'' &= \sum_j i\Delta f_{Pj}'' \exp. 2\pi i (hx_{Pj} + ky_{Pj} + lz_{Pj}) \\ &= |F_P''| \exp. i\alpha_P'' \end{aligned} \tag{7}$$

In the above equations (x_{Qk}, y_{Qk}, z_{Qk}) refer to the position-co-ordinates of the Q non-anomalous scatterers. In each case the minor suffix assumes values $k = 1$ to Q and $j = 1$ to P as the case may be.

As is obvious, the structure factor consists of four components. The first component F_Q^0 arises from the scattering powers f_{Qk}^0 of the

Q-non-anomalous scatterers and may be called the non-anomalous vector. The second component F_P^0 arises from the normal scattering f_{Pj}^0 of the P-anomalous scatterers and may be called the 'normal' vector. The third arises from $\Delta f_{Pj}'$ the real part correction to the atomic scattering factors and may be called the 'anomalous real' vector. The fourth component arises from the imaginary component $\Delta f_{Pj}''$ and may be called the 'anomalous imaginary' vector. All the four together define F_N the 'anomalous' structure factor. The first three components alone define F_N' the total contribution from the real parts of the scattering powers of all the atoms and may be called the total 'real' structure factor. The first two alone define the contribution from the f_j^0 of all the N-atoms, that is, from both the anomalous and non-anomalous scatterers. It will be called the 'normal' structure factor and will be denoted by F_N^0.

The intensity at the first wavelength will be given by

$$F_N F_N^* = |F_N|^2.$$

Thus,

$$\begin{aligned} |F_N|^2 &= (F_N^0 + F_P' + F_P'')(F_N^{0*} + F_P'^* + F_P''^*) \\ &= |F_N^0|^2 + |F_P'|^2 + |F_P''|^2 + 2|F_N^0||F_P'|\cos\psi^0 \\ &\quad + 2|F_P'||F_P''|\cos\epsilon + 2|F_N^0||F_P''|\cos\theta^0 \quad (8) \end{aligned}$$

where ψ, ϵ and θ are the angles between the vectors (F_N^0, F_P'), (F_P', F_P'') and (F_N^0, F_P'') respectively. They are given by

$$\psi^0 = \alpha_N^0 - \alpha_P'; \quad \epsilon = \alpha_P' - \alpha_P''; \quad \theta^0 = \alpha_N^0 - \alpha_P'';$$

where α_N^0, α_P' and α_P'' are the phases of the three vectors F_N^0, F_P' and F_P''. In general, there is no simple relationship between α_P'' and α_P', but if all the atoms in the group of P-anomalous scatterers are crystallographically equivalent then the phase angle α_P' is the same as the phase angle α_P^0 of F_P^0 and the phase angle α_P'' just leads α_P^0 by $\pi/2$. Usually, for a given wavelength it is highly improbable that there are more than one kind of scatterers for which the anomalous dispersion components are significant. Therefore, for the rest of the paper, we will be only concerned with the case of P-crystallographically equivalent anomalous scatterers. The theory for the general case, however, is given in the Appendix.

In this case, $\epsilon = \pi/2$ whence

$$\begin{aligned} |F_N|^2 &= |F_N^0|^2 + |F_P'|^2 + |F_P''|^2 + 2|F_N^0||F_P'|\cos\psi^0 \\ &\quad + 2|F_N^0||F_P''|\cos\theta^0. \quad (9) \end{aligned}$$

The intensity of the inverse reflection will be given by

$$|\bar{F}_N|^2 = \bar{F}_N \bar{F}_N^*$$

$$= (\bar{F}_N^0 + \bar{F}_P' + \bar{F}_P'')(\bar{F}_N^{0*} + \bar{F}_P'^* + \bar{F}_P''^*).$$

It is obvious from equations (4), (5), (6) and (7) that

$$\bar{F}_N^0 = F_N^{0*} \quad \text{and} \quad \bar{F}_P' = F_P'^* \quad \text{but} \quad \bar{F}_P'' = -F_P''^*$$

whence

$$|\bar{F}_N|^2 = |F_N^0|^2 + |F_P'|^2 + |F_P''|^2 + 2|F_N^0||F_P'|\cos\psi^0 - 2|F_N^0||F_P''|\cos\theta^0. \tag{10}$$

It is obvious from equations (8) and (10) that the intensities $|F_N|^2$ and $|\bar{F}_N|^2$ of the pair of inverse reflections *hkl* and $\bar{h}\bar{k}\bar{l}$ will be different. The difference between the two is given by

$$\Delta|F|^2 = 4|F_N^0||F_P''|\cos\theta^0. \tag{11}$$

The sum of the two is given by

$$S|F|^2 = 2|F_N^0|^2 + 2|F_P'|^2 + 2|F_P''|^2 + 4|F_N^0||F_P'|\cos\psi^0. \tag{12}$$

Equations (11) and (12) show that the angles θ^0 and ψ^0 can be obtained from an experimental measurement of $\Delta|F|^2$, $S|F|^2$ and $|F_N^0|^2$, provided the quantities $|F_P'|^2$ and $|F_P''|^2$ are known. The quantities $\Delta|F|^2$ and $S|F|^2$ can be obtained by measuring the intensities of the pairs of inverse reflections *hkl* and $\bar{h}\bar{k}\bar{l}$ at the first wavelength λ_1. The quantities $|F_N^0|^2$ can be obtained by measuring the intensities of the reflections at the second wavelength λ_2. (It must be noted that only at the first wavelength are the intensities $|F_N|^2$ and $|\bar{F}_N|^2$ different.) The quantities $|F_P'|$ and $|F_P''|$ can be obtained provided the positions and scattering factors of the atoms P are known. Usually the anomalous scatterers are found to be heavy atoms so that their positions can be fixed without much difficulty from the Patterson synthesis, which can be calculated from the intensity data alone. Thus it is possible to obtain the quantities $\cos\theta^0$ and $\cos\psi^0$ and hence the phase angle α_N^0. Since an angle derived from a cosine can have a sign either *plus* or *minus*, two pairs of values will be obtained for α_N^0, the first

pair from $\cos\theta^0$ and the second pair from $\cos\psi^0$. These two pairs of values are given by

$$\alpha_N^{0\,(1,2)} = \frac{\pi}{2} + \alpha_P^0 \pm \theta^0 \tag{13}$$

$$\alpha_N^{0\,(3,4)} = \alpha_P^0 \pm \psi^0. \tag{14}$$

It will be found that one of the two possible values of the first pair will always agree with one of the two possible values of the second pair. This coincident value is the correct value of the phase angle α_N^0. Thus the phases of the complex structure factors of a non-centric crystal can be unambiguously obtained from an experimental measurement of the X-ray intensities at two incident wavelengths.

The above method can be applied to determine the structure of centrosymmetric crystals also. In this case, as is well known, the phase angle α_N^0 can be only either 0 or π so that it is only necessary to determine the *plus* or *minus* sign of the structure factor. It is obvious that θ^0 is $\pi/2$ (because $\alpha_N^0 = 0$ or π and so also is α_P^0), so that $\Delta\,|\,F\,|^2$ is zero and $S\,|\,F\,|^2$ reduces to

$$S\,|\,F\,|^2 = 2\,|\,F_N^0\,|^2 + 2\,|\,F_P'\,|^2 + 2\,|\,F_P''\,|^2 + 4\,F_N^0\,.\,F_P'. \tag{15}$$

Equation (15) can be used to determine the sign of F_N^0 provided that the sign of F_P' is known. It is to be noted that the principle of the method in this case is identical with that of the isomorphous replacement method developed and extensively used by Robertson (1936).

3. Theory of the One Wavelength Anomalous Dispersion Method

The above discussion shows that the phases of the structure factors can be uniquely determined from an experimental measurement of the intensities at two suitable wavelengths λ_1 and λ_2. One may not always be fortunate enough to secure two such wavelengths. Therefore, we will now consider the possibilities of phase determination when only the first wavelength is available. (It must be noted that when the second wavelength alone is available, phase determination along these lines is not possible.) In this case, it is possible to obtain only the intensities $|\,F_N\,|^2$ and $|\,\overline{F_N}\,|^2$, but not $|\,F_N^0\,|^2$. Therefore, it will be possible to obtain only the angle θ' between F_P'' and F_N' the total real vector and not the angle θ^0. It is obvious that in this case the valid equations are (Ramachandran and Raman, 1956)

$$\Delta\,|\,F\,|^2 = 4\,|\,F_N'\,|\,|\,F_P''\,|\cos\theta' \tag{16}$$

$$S\,|\,F\,|^2 = 2\,|\,F_N'\,|^2 + 2\,|\,F_P''\,|^2. \tag{17}$$

Equations (16) and (17) show that the angle θ' can be obtained from an experimental measurement of $|F|^2$ and $|\bar{F}|^2$ provided the positions of the P-atoms are known, so that $|F_P''|^2$ can be calculated. But the angle θ' derived from a cosine may have a sign either *plus* or *minus* so that two values are possible for the phase angle α_N' given by

$$\alpha_{1,2} = \frac{\pi}{2} + \alpha_P^0 \pm \theta.$$

Thus, if one value be α, the other value is given by $\pi + 2\alpha_P^0 - \alpha$, so that the two solutions are antisymmetric with respect to the phase α_P^0 of the contribution from the anomalous scatterers.

This inherent two-fold ambiguity can be resolved in a number of ways but even if the ambiguity cannot be resolved the use of both the solutions leads only to the double-phased synthesis, termed the anomalous synthesis (Raman, 1957), which gives just the structure against a background which is negative. These points have already been indicated in an earlier paper (Raman, 1957) and will be discussed in greater detail in a different context (Ramachandran and Raman, 1959).

4. Theory of the Real Component Method

In this section will be discussed the possibilities of phase determination when two wavelengths are available such that one of them (λ_1) is slightly longer than the absorption limit (λ_P) of a group of P-atoms so that $\Delta f'$ alone comes into play and the other wavelength λ_2 is far away from λ_P so that $\Delta f'$ is negligible. In this case, it is possible to obtain the angle ψ' between F_P' and F_N' from a measurement of the intensities $|F_N'|^2$ and $|F_N^0|^2$ at the two wavelenghts λ_1 and λ_2. The relevant equation is

$$|F_N'|^2 = |F_N^0|^2 + |F_P'|^2 + 2|F_N^0||F_P'| \cos \psi'. \qquad (18)$$

But here again, the phase determination is ambiguous even though the intensities have been measured at two wavelengths. Two values are possible for the phase angle α_N^0, given by

$$\alpha_{1,2} = \alpha_P^0 \pm \psi'.$$

Thus, if one value be α, then the other is given by $2\alpha_P^0 - \alpha$ so that the two solutions are symmetrical with respect to α_P^0. The use of both the solutions leads to the double-phased synthesis called the isomorphous synthesis which gives the structure against a positive background (Raman, 1957).

It may be noted that this method is identical in principle with the isomorphous single replacement method of Bijvoet (1951). It is inferior to

the single wavelength method described in the previous section in three ways. Firstly, it demands measurements of intensities at two wavelengths. Secondly, because of the positivity of the background of the double-phased synthesis, it will not be possible to resolve the structure peaks from the spurious background peaks. On the other hand, the background peaks of the anomalous synthesis obtained in the one wavelength method show up only as negative peaks and therefore can be distinguished from the structure peaks and eliminated. Thirdly, the real component method will not determine the absolute configuration whereas the one wavelength imaginary component method will determine not merely the structure but the absolute configuration as well.

5. Unique Determination of Phase Angles

Thus we have discussed three different methods of determining the phases of structure factors of non-centrosymmetric crystals. Of the three methods, only the first method leads to a unique solution. The other two methods lead to ambiguous solutions. The ambiguity can be resolved in a number of ways by combining the different techniques among themselves and also with the isomorphous replacement technique (Bijvoet, 1951) and the heavy atom technique (Lipson and Cochran, 1953). We will here give a short summary of the possible methods of resolving the ambiguity.

(*a*) *One crystal, two wavelengths: Method I.*—This is the same as the generalised method discussed in Section 2. It consists in measuring the intensities at two wavelenghts λ_1 and λ_2. λ_1 is chosen to be slightly smaller than the absorption limit of a group of atoms A so that both $\Delta f'$ and $\Delta f''$ are significant. λ_2 is chosen to be either much larger or much smaller than λ_A so that both are negligible. The first measurement gives the Bijvoet inequalities.

(*b*) *One crystal, two wavelengths: Method II.*—This is a variation of Method I. It may happen that a wavelength of type λ_2 is not available but instead, a different wavelength λ_3 is available, this being such that $\Delta f''$ of a second group of atoms B is significant. It is obvious that the measurement at λ_1 will give a pair of solutions antisymmetric with respect to α_A, while the measurement at λ_3 will give a pair of solutions antisymmetric with respect to α_B. Combining the two, a unique solution can be obtained.

(*c*) *One crystal, three wavelengths: Method III.*—In this case, measurements are made at three wavelengths λ_1, λ_2 and λ_3. λ_1 is so chosen that $\Delta f'$ of a group of atoms A is significant, λ_2 is so chosen that $\Delta f'$ of a different group B is significant and λ_3 is so chosen that both are negligible.

Measurements 1 and 3 together will give a pair of solutions symmetrical with respect to α_A and measurements 2 and 3 together will give a pair of solutions symmetrical with respect to α_B, whence the unique solution can be obtained. This is a purely real component method, so that λ_1 and λ_2 must lie slightly to the long wavelength side of the absorption limits of the groups of atoms A and B.

(*d*) *Two crystals, one wavelength : Method IV.*—In this method, we combine the imaginary component method with the isomorphous replacement technique. As the name implies, measurements are made with two crystals at one wavelength. The two crystals chosen are a pair of isomorphs C_1 and C_2. The difference between C_1 and C_2 is that a group of P atoms of C_1 have been replaced by P others in C_2. The diffraction wavelength chosen is such that $\Delta f''$ of a group of atoms A is significant. The group A may be the same as P, as often happens, or may be different. If the two are the same, then Friedel's law is violated in the case of one crystal only. If different, it is violated in the case of both crystals. The measurement of intensity-differences between pairs of inverse reflections will give a pair of solutions for α_N' antisymmetric with respect to α_A'. Measurement of intensity-differences between corresponding reflections from the two crystals will give a pair of solutions symmetrical with respect to α_P. Combining the two, the unique solution can be obtained.

(*e*) *Two crystals, two wavelengths : Method V.*—In this method we combine the isomorphous replacement technique with the anomalous real component method. The case envisaged is that of a pair of isomorphous crystals with a group of replaceable atoms P and a pair of wavelengths so chosen that the real component $\Delta f'$ of a group of atoms B is significant for the first wavelength and negligible for the second wavelength. It is essential that group B is different from group P. Intensity measurements will have to be made with the first wavelength for both crystals and with the second wavelength for any one crystal. The intensity-differences of corresponding reflections of the two crystals as measured with the same wavelength will give a pair of solutions symmetrical with respect to α_P, while the intensity-differences from the same crystals but obtained with two different wavelengths will give a second pair of solutions symmetrical with respect to α_B, whence the unique solution can be obtained by combining the two.

(*f*) *Three crystals, one wavelength : Method VI.*—This is a purely isomorphous replacement method. It is nothing but the double replacement technique of Harker (1956) and Perutz (1956).

The case envisaged is that of three crystals C_1, C_2 and C_3. C_1 and C differ in that A of the atoms of C_1 have been replaced by A others in C_2 without unduly distorting the overall crystal structure. C_1 and C_3 differ in that a different set of atoms B of C_1 have been isomorphously replaced by B others in C_3. Intensity-differences between C_1 and C_2 give a pair of solutions symmetrical with respect to α_A while those between C_1 and C_3 give a different pair symmetrical with respect to α_B. It is obvious that Methods V and VI will fail if the groups B and A are both centrosymmetric. Then the two pairs of values will be coincident and the ambiguity cannot be resolved.

(*g*) *One crystal, one wavelength or the quasi-heavy atom method : Method VII.*—Finally we may consider the simplest but probably the most powerful of all, namely, the one crystal, one wavelength method. It consists in combining the anomalous imaginary component method with the usual idea of the heavy atom method. The former method gives a pair o solutions antisymmetric with respect to the phase α_P of the contribution from the anomalous scatterers. One of the two values will always be nearer to α_P than the other and the nearer value can be taken to be the correct value and used to calculate a preliminary Fourier synthesis. An approximate structure can then be derived from this diagram and the phase angles recalculated from the assumed co-ordinates. Thus the ambiguity can be completely resolved. The justification for this procedure comes from the fact that anomalous scatterers are usually heavy atoms so that their contribution towards the structure factor plays a prominent part in building up the latter. Thus the procedure will be in general correct, particularly for those reflections for which the contribution from the anomalous scatterers is fairly large. The structure of lysine hydrochloride has been solved by this method (Raman, 1959).

6. A Comparison of the Different Methods

The above discussion shows that there are a number of methods available for uniquely determining the phases of the structure factors of a non-centric crystal. However, not all the ideas are practically feasible. Most of them have been discussed here for the sake of completeness. It is interesting that all the methods are based on the same principle, namely, the fact that it is possible to determine the phases of the structure factors by varying the scattering power at one or more points in the unit cell and studying the corresponding changes in the X-ray intensities. In the single crystal, multiple wavelength methods, this variation is produced by altering the wavelength

of excitation, whereas in the multiple crystal, single wavelength methods, the variation is produced by replacing some of the atoms by chemical means.

The latter are inferior to the former in that chemical substitution may disturb atomic positions so that the observed intensity-differences cannot be solely attributed to changes in scattering powers. Further, reduction of data to absolute scale is also more difficult. It is always easier to reduce the data from the same crystal to absolute scale than those from different crystals. But these disadvantages are offset by the fact that in the replacement techniques, the magnitude of the intensity-difference is much more than those in the anomalous dispersion methods. In the latter, the effects are due to $\Delta f'$ or $\Delta f''$, quantities which are quite small. Further, the anomalous dispersion methods suffer from the fact that they lack generality. They can be adopted only if anomalous scatterers are present and only if suitable wavelengths are available. In fact, they fail miserably in the case of purely C, N, O compounds. The K absorption edges of these atoms lie far out on the long wavelength side of even the longest available radiation, *viz.*, MnKα. On the other hand, the isomorphous replacement method can be applied even to such cases.

However, when conditions permit, the obvious choice is for the one crystal, one wavelength method. In this method the advantages of measurement with one crystal, antisymmetrical solutions with the accompanying possibility of resolution of the ambiguity by the quasi-heavy atom method and finally the possibility of simultaneously determining the structure and absolute configuration are all blended together.

7. Summary

It is possible to determine the phases of X-ray reflections given by a non-centrosymmetric crystal, provided it contains an atom or a group of atoms which exhibit anomalous dispersion for the incident X-radiation. Both the change in the real part ($\Delta f'$) as well as the presence of the imaginary part ($i\Delta f''$) in the scattering power can be used for this purpose—either one alone or both together. In the former case, the phase determination is ambigouus but it becomes unique if both are used.

Still more general methods may be considered, using two or three different wavelengths and also combining this technique with the well-known isomorphous replacement technique—single or double replacement. All these methods are discussed in this paper and their relative merits are pointed out.

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APPENDIX

We will here consider the phase relationships between the vectors F_P^0, F_P' and F_P'' when the P-anomalous scatterers are equivalent and prove that $\alpha_P' = \alpha_P$ and $\alpha_P'' = \pi/2 + \alpha_P^0$. In general, when the P-atoms are not equivalent, then the vectors are given by equations (5), (6) and (7). If they are equivalent, then it is obvious that $\Delta f''_{P_1} = \Delta f''_{P_2} \ldots = \Delta f_P''$ and similar relations are true for $\Delta f_{Pj}'$ and f_{Pj}^0 also. Thus, in this case, the minor suffix loses its significance and the vectors are given by just multiplying f_P^0, $\Delta f_P'$ and $\Delta f_P''$ by PT where P is the symmetry number of the space group and T is the trigonometric expression to which the exponent of the equations (5), (6) and (7) will reduce when summed over the P-equivalent atoms. Thus one obtains the equations:

$$F_P^0 = f_P^0 \,.\, \mathbf{PT}; \quad F_P' = \Delta f_P' \,.\, \mathbf{PT}$$

and

$$F_P'' = i\Delta f'' \cdot \mathbf{PT}.$$

From these equations, it follows that:

$$F_P' = \left(\frac{\Delta f_P'}{f_P^0}\right) F_P^0;$$

$$F_P'' = \left(\frac{\Delta f''}{f_P^0}\right) \left(\exp. \frac{i\pi}{2}\right) F_P^0$$

whence

$$\alpha_P' = \alpha_P^0 \quad \text{and} \quad \alpha_P'' = \frac{\pi}{2} + \alpha_P^0.$$

If the P-atoms are not equivalent the phase of F_P' is given by some angle α_P' and the phase of F_P'' by some other angle α_P''. α_P' and α_P'' can be obtained from equations (6) and (7), provided the positions of the P-atoms are known. It is convenient to put α_P'' in the form of $\pi/2 + \phi$ so that in the special case of P-equivalent atoms ϕ becomes α_P^0. Thus the theory for the general case can be obtained from the theory of the special case by putting α_P' for α_P^0 in F_P' and ϕ for α_P^0 in F_P''.

THE MICROWAVE SPECTRUM OF METHYL CYANIDE AND *l*-TYPE DOUBLING IN CH_3CN, CH_3NC, CH_3CCH AND CF_3CCH

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Abstract

The microwave spectrum of Methyl cyanide molecule has been obtained corresponding to the transitions $J = 0 \rightarrow 1$, $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ in the ground vibrational state as well as in the excited degenerate vibrational states $v_8 = 1$ and $v_8 = 2$. The frequencies of the lines are measured by using a secondary standard spectrograph taking mostly the ammonia lines as standards. The value of the vibration-rotation interaction constant α_8 has been found to be $-27{\cdot}3 \pm 0{\cdot}4$ mc./sec. The spectrum obtained for the transitions $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ with $v_8 = 1$ has been understood on the basis of Nielsen's theory of *l*-type doubling in symmetric top molecules. The assignments give a value of 0·94 for the coriolis interaction constant which is consistent with the value obtained from the infra-red spectral data.

The earlier work on similar transitions involving *l*-type doubling in the molecules CH_3NC, CH_3CCH and CF_3CCH has been reviewed and the inconsistencies in the values of some parameters like coriolis interaction constant ζ and the rotation constant D_{JK} obtained by earlier workers from their assignments are pointed out. A reassignment of the transitions and the involved parameters removes these inconsistencies and yields coriolis interaction constants which are in close agreement with those obtained from infra-red spectral data. The following are the different ζ values obtained:

$$\zeta_8 \text{ in } CH_3NC = 0{\cdot}93$$

$$\zeta_{10} \text{ in } CH_3CCH = 1{\cdot}00$$

$$\zeta_9 \text{ in } CH_3CCH = 0{\cdot}95$$

$$\zeta_{10} \text{ in } CF_3CCH = 0{\cdot}6$$

Introduction

Methyl cyanide molecule has a trifold axis of symmetry and belongs to the point group C_{3v}. This molecule has eight fundamental vibrations of which

four are totally symmetric and four are doubly degenerate. The degenerate fundamental v_8 is the lowest and lies at 361 cm.$^{-1}$ [1, 2, 3]. As the Boltzman factor corresponding to this frequency will be large enough, an appreciable number of molecules are expected to be in the excited state $v_8 = 1$ at the room temperature. A lesser number of the molecules may also be expected to lie in the excited state corresponding to the overtone vibration $v_8 = 2$. Thus the microwave spectral lines corresponding to the pure rotational transitions in the ground vibrational state as well as in the excited states $v_8 = 1$ and $v_8 = 2$ can be expected to be easily observed at room temperature with the decreasing order of intensity. A study of the rotational transitions of the molecule in excited vibrational states is expected to give information about the vibration-rotation interaction in the molecule.

The microwave spectra of CH_3CN and CH_3NC were first obtained by Ring, Edward, Kessler and Gordy[4] and were later worked out in more detail by Kessler, Ring, Trambarulo and Gordy.[5] They observed the rotational transitions $J = 0 \rightarrow 1$ in the ground vibrational state $v_8 = 0$ and $J = 1 \rightarrow 2$ in the states $v_8 = 0$ and $v_8 = 1$. In the present work the transitions $J = 0 \rightarrow 1$, $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ are observed in all the vibrational states $v_8 = 0$, $v_8 = 1$ and $v_8 = 2$.

Experimental Procedure

The observations were made with two different 100 kc. stark modulation spectrographs using voltages ranging from 25–400 volts. The construction of these spectrographs is similar to that of the spectrographs described by earlier workers.[6] A 12′ stark cell of an X-band copper wave-guide was used up to 37,000 mc. and a 3′ stark cell of K-band coin silver wave-guide was used for 55,000 mc. region.

A Raytheon klystron type QK-306 was used for the observations of the $J = 0 \rightarrow 1$ transitions and type QK-292 was used for the $J = 1 \rightarrow 2$ transitions. The microwave radiation in the region 55,000 mc. needed for the study of the $J = 2 \rightarrow 3$ transitions was obtained by the harmonic generation method. A $J \rightarrow I$ multiplier made for this purpose is shown in Fig. 1 and it is similar in construction to the $K \rightarrow I$ multipliers used by earlier workers.[7] A slotted sylvania crystal 1N26 has been used as a multiplier and a Raytheon klystron type QK-289 working in the region 27,270–30,000 mc. has been used as the primary source of microwave radiation.

The sylvania type 1N26 crystals were used for the detection of the lines in the K-band region and sylvania type 1N53 crystals for higher frequency regions. The energy signal was taken from the detector to a phase sensitive

lock-in amplifier which was coupled to a phase shift amplifier, both of which were tuned to 100 kc. fundamental frequency of the square wave generator.[7] The spectral lines were recorded by using an Esterline-Angus dc. milliammeter recorder. In this phase sensitive recording arrangement the spectral lines are recorded such that stark components point downwards and zero field lines point upwards.

The frequencies were measured* by employing a Hallicrafter receiver type SX-62A to measure the beat between two oscillators one of which is stabilized at the frequency of the known NH_3 line (within the range of about 110 mc. from the search line) while the other at the line to be measured.[8] The range could be increased still further by mixing a signal from a calibrated r-f. General Radio Signal Generator type GR-1001A with the beat between the two klystrons. The output from the receiver which appears as a marker is superimposed upon the spectral line whose frequency is to be measured. The receiver setting is adjusted so that the marker coincides with the centre of the spectral line. The receiver and the signal generator used for this purpose were calibrated with the help of a General Radio frequency Heterodyne meter and Calibrator type GR-620A.

RESULTS

Figure 2 shows the high speed recording of the spectrum for the transitions $J = 0 \rightarrow 1$ in ground vibrational state and in the excited vibrational states $v_8 = 1$ and $v_8 = 2$ in which the decreasing order of the intensity in the three transitions can be noted.

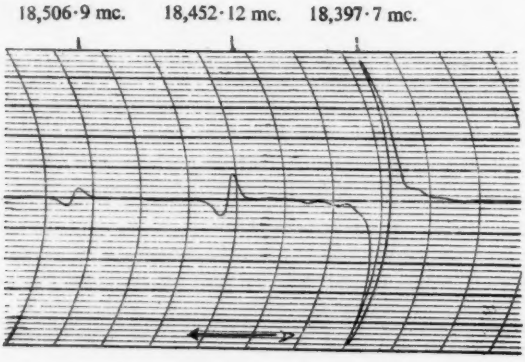

FIG. 2. Recorder tracing of the lines corresponding to the transitions $J = 0 \rightarrow 1$ with $v_8 = 0$, $v_8 = 1$ and $v_8 = 2$. Stark components point downwards and zero field lines point upwards.

* Details given separately by K. V. L. N. Sastry.[9]

Figure 3 shows the slow speed recording of the line $J = 0 \rightarrow 1$ in the ground vibrational state indicating probably the hyperfine splitting into 3 components which arise because of the nuclear quadrupole coupling constant for nitrogen atom.

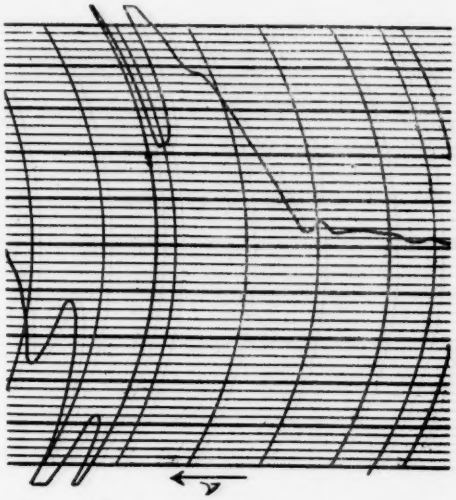

FIG. 3. Slow speed recording of the line $J = 0 \rightarrow 1$ in the ground state (18,397·7 mc.).

Figure 4 shows the lines corresponding to the transitions $J = 1 \rightarrow 2$ in the ground vibrational state and in the excited vibrational states $v_8 = 1$ and $v_8 = 2$. The line corresponding to the transition in the excited vibrational state $v_8 = 1$ is split into three components, while the line corresponding to the transition in the excited state $v_8 = 2$ remains single.

Figure 5 shows the lines corresponding to the transition $J = 2 \rightarrow 3$ in the ground vibrational state and in the excited states $v_8 = 1$ and $v_8 = 2$. Here again the transition corresponding to the molecules in the excited state $v_8 = 1$ shows 3 main components, but a slow speed recording (Fig. 6) shows that the middle component is further split into three components. Thus there are in all five lines for the transition $J = 2 \rightarrow 3$ in the excited vibrational state $v_8 = 1$. The transition $J = 2 \rightarrow 3$ in the excited vibrational state $v_8 = 2$ shows only one line.

Figure 7 shows the slow speed recording of the $J = 2 \rightarrow 3$ transition in the ground vibrational state. The structure probably represents the superimposed partially resolved K-structure and partially resolved hyperfine structure.

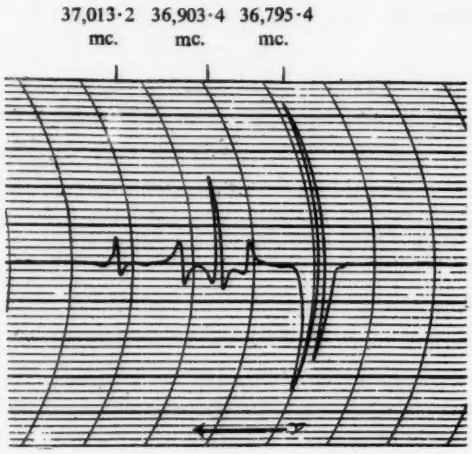

FIG. 4. Recording of the lines corresponding to the transitions $J = 1 \rightarrow 2$ with $v_8 = 0$, $v_8 = 1$ and $v_8 = 2$.

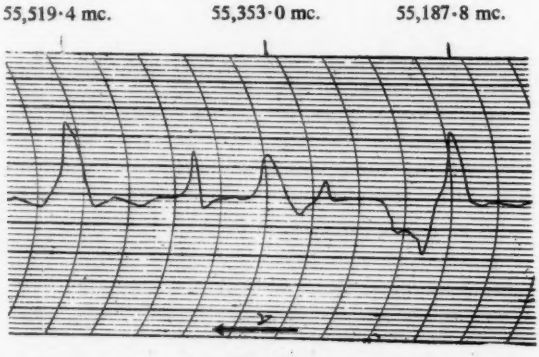

FIG. 5. Recording of the lines corresponding to the transition $J = 2 \rightarrow 3$ in the ground state and in the excited states $v_8 = 1$ and $v_8 = 2$.

The frequencies of the spectral lines observed and measured for the first time in the present experiments are listed in Table I. Further the known frequencies of the lines measured by earlier workers[4, 5] and also observed in the present experiments are included in the Table.

Kessler *et al.*[5] determined the structure of methyl cyanide molecule from their microwave spectral data of the different isotopic species of the molecule in the ground vibrational state. We will discuss here only the information that one can obtain from the spectral data in the excited vibrational states.

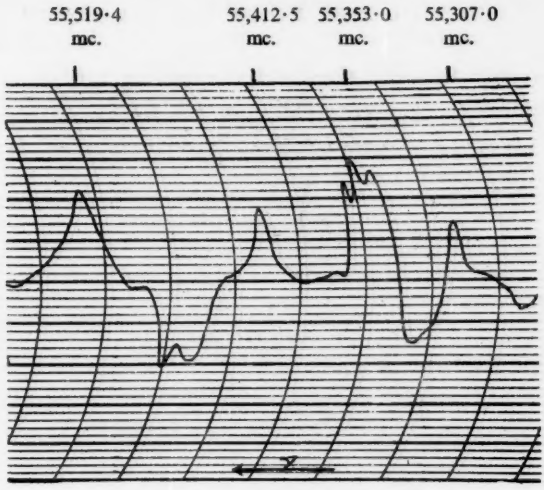

FIG. 6. Slow speed recording of the lines corresponding to the transition $J = 2 \rightarrow 3$ with $v_8 = 1$ and $v_8 = 2$.

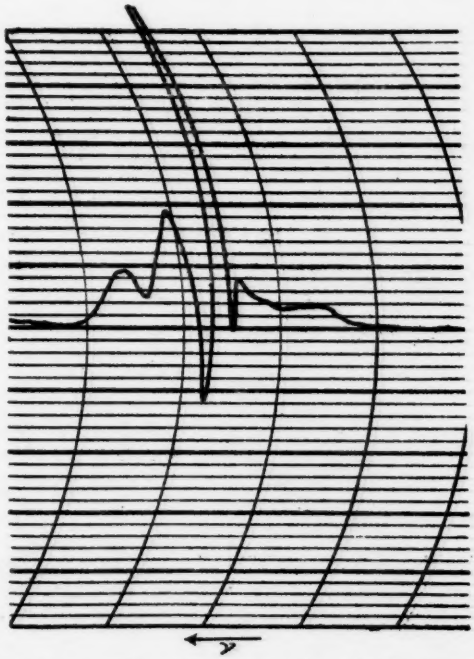

FIG. 7. Slow speed recording of the line $J = 2 \rightarrow 3$ in the ground state (55,187·8 mc.).

The vibration-rotation interaction constant α_8 can be determined in a number of ways by taking the proper differences between the frequencies of the rotational lines corresponding to the ground vibrational state and the other excited vibrational states. Making use of the differences for the transitions $J = 0 \rightarrow 1$, $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ in the ground state and the

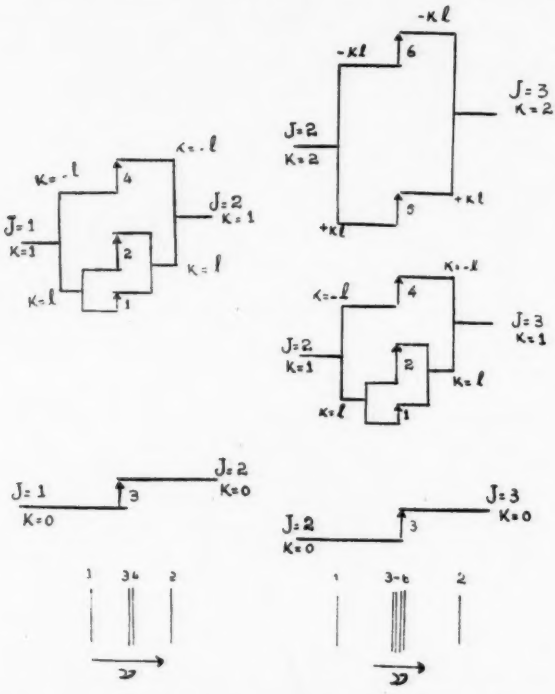

FIG. 8 *a*. Rotational levels of a symmetric top molecule for J = 1 and J = 2 showing *l*-type doubling, when the molecule is in a vibrational state $v_i = 1$ with $l = 1$. The expected microwave spectral pattern is also shown.

FIG. 8 *b*. Rotational levels of a symmetric top molecule for J = 2 and J = 3 showing *l*-type doubling, when the molecule is in a vibrational state $v_i = 1$ with $l = 1$. The expected microwave spectral pattern is also shown.

excited state $v_8 = 2$, one gets $-27{\cdot}3$, $-27{\cdot}2$ and $-27{\cdot}6$ mc./sec. respectively. α_8 calculated by taking the difference between the frequency of $J = 0 \rightarrow 1$ transition in the ground vibrational state and the excited vibrational state $v_8 = 1$ comes out to be $-27{\cdot}25$ mc./sec. The average of these four values comes out to be $-27{\cdot}3$ mc./sec. The error involved in the determination of α_8 is probably not more than $\pm 0{\cdot}4$ mc./sec. This value

TABLE I

Observed frequencies for the pure rotational transitions of methyl cyanide

J	Vibrational state	Frequencies[a] in mc.	Reference
$0 \rightarrow 1$	Ground	18,396·3 18,397·7 18,399·8	Ring *et al.*[4]
	$v_8 = 1$	18,452·2	Present work
	$v_8 = 2$	18,506·9	Present work
$1 \rightarrow 2$	Ground	36,793·64 36,794·26 36,794·88 36,795·38 36,796·27 36,797·52	Kessler *et al.*[5]
	$v_8 = 1$	36,870·94 36,903·40 36,942·15	Kessler *et al.*
	$v_8 = 2$	37,013·2	Present work
$2 \rightarrow 3$	Ground[b]	55,192·8 55,187·8	Present work
	$v_8 = 1$	55,307·0 55,344·9 55,353·0 55,359·5 55,412·5	Present work
	$v_8 = 2$	55,519·4	Present work

[a] The lines $J = 0 \rightarrow 1$ with $v_8 = 1$ and $v_8 = 2$ are measured by taking the ammonia line at 18499·50 mc. as standard. The line $J = 1 \rightarrow 2$ with $v_8 = 2$ is measured with the CH_3CN line at 36,942·15 mc. as standard. The $J = 2 \rightarrow 3$ lines in the ground state are measured with the ammonia line at 27,478·00 mc. as standard and the lines corresponding to $J = 2 \rightarrow 3$ in $v_8 = 1$ and $v_8 = 2$ are measured with the NH_3 line at 27,772·52 mc. as standard.

[b] The slow speed recording of the spectrum corresponding to the transition $J = 2 \rightarrow 3$ in the ground state shows clearly three components (*see* Fig. 6) of which, however, only two could be seen properly on the oscilloscope and are therefore measured as such. These two probably represent the two strong components.

of a_8 is also consistent with the average value that one gets from the position of the central lines corresponding to the $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ transitions with $v_8 = 1$. It may be noted that the value $-22{\cdot}5$ mc./sec. obtained earlier for a_8 by Coles, Good and Hughes[10] appears to be improbable.

DISCUSSION

In order to explain the spectral pattern obtained by Kessler *et al.*[5] for the $J = 1 \rightarrow 2$ transition in the vibrational state $v_8 = 1$ for CH_3CN as well as for CH_3NC, Nielsen[11] developed the theory of *l*-type doubling in symmetric top molecules. His theory predicts for the above transition in CH_3CN molecule, a set of four lines, two of which will lie close together in between other two lines which will be more widely separated. The spectrum obtained for CH_3CN by Kessler *et al.*[5] and also confirmed in the present experiments shows for this transition two lines separated by 71·2 mc. with a single line in between at a distance of 32·5 mc. from the position of the low frequency component. Assuming that the central two lines expected are too close to be resolved, the Nielsen's theory is in general good qualitative agreement with the observed pattern. But the molecular constants obtained by Nielsen[11] from his theory by using the above experimental data are rather improbable. He obtained a value of $-$ 0·4 mc./sec. for the rotational constant D_{JK} and a value of $-$ 0·5 for the coriolis interaction constant ζ_8. The rotational constant D_{JK} for the ground vibrational state is known from the data of Kessler *et al.*[5] to be 0·18 mc./sec. but it is not known for the excited vibrational state $v_8 = 1$. Its value for the excited state can be expected to be different[12] from that in the ground state, but probably not to that extent as to change from 0·18 mc./sec. in the ground state to $-$ 0·4 mc./sec. in the excited state. The infra-red spectrum of CH_3CN obtained by Venkateswarlu[1, 2] and later by other workers[3, 13] shows that the coriolis interaction constant ζ_8 should be positive and definitely not negative. The value for ζ_8 obtained by Venkateswarlu[1, 2] is 0·95 while that obtained by Thompson and Williams[3] is 0·99. The data given by Parker, Nielsen and Fletcher[13] yield $\zeta_8 = 0{\cdot}93$. We will now proceed to go into Nielsen's theory in some detail in general and then understand the experimental patterns obtained for the $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ transitions using molecular parameters without the above inconsistencies.

THE THEORY OF THE *l*-TYPE DOUBLING IN MOLECULES BELONGING TO THE POINT GROUP C_{3v}

The rotational energy levels (with $K \neq 0$) of a symmetric top molecule in a doubly degenerate vibrational state, are known to be split into two because of the coriolis interaction. The splitting is given by $4Kl\zeta A_v$ where A_v is a rotational constant in the vibrational state, ζ is the coriolis interaction constant, K is the rotational quantum number of the level and l is the quantum number of vibrational angular momentum. Here l takes the values

$v, v-2, \ldots, 1$ or 0, where v is the quantum number of the degenerate vibration.

When ζ is positive, the level having a positive value for Kl will be lower than that having a negative value. Herzberg[14] designates the level with a positive value of Kl as $+l$ level and the other as $-l$ level. Following the earlier work of Wilson,[15] Herzberg[14] has shown that when $|K| = 3p+1$ where p is an integer including zero, the level with a positive value of Kl represents two coinciding levels of species A and the level with a negative value of Kl represents a doubly degenerate level of species E. The reverse will be the case when $|K| = 3p+2$. When $|K| = 3p$, each of the two levels (the one with positive value of Kl as well as the other with the negative value of Kl) represents separately a degenerate level of species E. The degeneracy of the rotational levels of species E persists even if all interactions are taken into account, whereas the pairs of coinciding levels of species A may split (Wilson, reference 15). This kind of splitting of the coinciding levels of species A is called K-type doubling by Herzberg in his book. But later Nielsen who has developed a detailed theory[11] of this splitting refers to it as l-type doubling.

Nielsen has shown that this splitting is appreciable for the levels with $|K| = 1$ only, and that it is negligibly small for those with $|K|$ greater than 1. The energy level diagrams for the transitions $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ with $v_8 = 1$ are shown in Figs. 8 *a* and 8 *b*.

According to the Nielsen's theory the rotational energy of a symmetric top molecule in the first excited degenerate bending state is given by the formula[16]

$$\begin{aligned} E_v = h\,[&B_v J(J+1) - (B_v - A_v)K^2 - 2Kl\zeta A_v - D_J J^2(J+1)^2 \\ &- D_{JK} J(J+1)K^2 - D_K K^4 + 2\{(2D_J + D_{JK})J(J+1) \\ &+ (2D_K + D_{JK})K^2\}Kl\zeta + P_{(J,K,l)}] \end{aligned} \tag{1}$$

where

$$P_{(J,K,l)} = \pm \tfrac{1}{2} J(J+1)q \qquad \text{for} \quad K = l = \pm 1 \tag{2a}$$

q being given by $(2B_e^2 a)/\omega_i$ in which a represents a coefficient slightly greater than 1, ω_i the frequency of the lowest degenerate fundamental vibration, and

$$P_{(J,K,l)} = \pm \frac{\{J(J+1) - K(K\mp 1)\}\{J(J+1) - (K\mp 1)(K\mp 2)\}q^2}{8(K\mp 1)\{(1-\zeta)A_v - B_v\}}$$

$$\text{for} \quad K \neq l = \pm 1 \tag{2b}$$

The other terms are the usual rotation constants of the molecule. The upper signs in equation (2 *b*) are to be taken when K and *l* have the same sign, while the lower signs are to be used when K and *l* are of different signs. In equation (2 *b*) the terms D_{JK} and D_J are neglected in comparison to B_v and A_v. The frequencies of the rotational transitions are given by

$$\nu = 2B_v(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 + 4(2D_J + D_{JK})Kl\zeta + \Delta P_{(J,K,l)} \qquad (3)$$

where

$$\Delta P_{(J,K,l)} = \pm (J+1)q \qquad \text{for} \quad K = l = \pm 1 \qquad (4\,a)$$

and

$$\Delta P_{(J,K,l)} = \pm \frac{[(J+1)\{(J+1)^2 - (K \mp 1)^2\}q^2]}{[4(K \mp 1)\{(1-\zeta)A_v - B_v\}]} \qquad \text{for} \quad K \neq l = \pm 1 \qquad (4\,b)$$

In equation (4 *b*) the upper signs correspond to the cases where K and *l* have the same sign, while the lower signs correspond to those where K and *l* are of different signs.

APPLICATION TO THE SPECTRUM OF CH_3CN

According to the above equations the transition $J = 1 \rightarrow 2$ in the excited bending vibrational state $v_8 = 1$ is expected to show a pair of closely spaced lines approximately midway between two other lines widely separated by $4q$. The positions of these four lines can be calculated to be at:

$$\left.\begin{aligned} &4B_v - 32D_J - \frac{(3q^2)}{[2\{(1-\zeta)A_v - B_v\}]} \quad \text{for } K = 0,\ l = \pm 1 \\ &4B_v - 32D_J - 4D_{JK} - 8(2D_J + D_{JK})\zeta \\ &\qquad\qquad \text{for } K = \pm 1,\ l = \mp 1 \\ &\left.\begin{aligned} &4B_v - 32D_J - 4D_{JK} + 8(2D_J + D_{JK})\zeta + 2q \\ &4B_v - 32D_J - 4D_{JK} + 8(2D_J + D_{JK})\zeta - 2q \end{aligned}\right\} \\ &\qquad\qquad \text{for } K = \pm 1,\ l = \pm 1 \end{aligned}\right\} \qquad (5)$$

As mentioned earlier the experimental pattern shows two lines widely separated by 71·2 mc./sec., with a single line in between them.

The transition $J = 2 \rightarrow 3$ with $v_8 = 1$ is expected to consist of four closely spaced lines approximately midway between two lines which should be $6q$ apart. The frequencies of these expected lines are given by

$$
\left.\begin{aligned}
&6B_v - 108D_J - \frac{6q^2}{(1-\zeta)A_v - B_v} && \text{for } K = 0,\ l = \pm 1\\
&6B_v - 108D_J - 6D_{JK} - 12(2D_J + D_{JK})\zeta\\
&\qquad - \frac{15q^2}{8[(1-\zeta)A_v - B_v} && \text{for } K = \pm 1,\ l = \mp 1\\
&5B_v - 108D_J - 24D_{JK} + 24(2D_J + D_{JK})\zeta\\
&\qquad + \frac{6q^2}{(1-\zeta)A_v - B_v} && \text{for } K = \pm 2,\ l = \pm 1\\
&6B_v - 108D_J - 24D_{JK} - 24(2D_J + D_{JK})\zeta\\
&\qquad && \text{for } K = \pm 2,\ l = \mp 1\\
&6B_v - 108D_J - 6D_{JK} + 12(2D_J + D_{JK})\zeta + 3q\\
&6B_v - 108D_J - 6D_{JK} + 12(2D_J + D_{JK})\zeta - 3q\\
&\qquad && \text{for } K = \pm 1,\ l = \pm 1
\end{aligned}\right\} \qquad (6)
$$

The present observations show that the spectrum consists of three closely spaced lines nearly midway between two lines which are 105·5 mc./sec. apart. Assuming that the two widely separated lines are represented by the last two of the six expressions of the equation (6), the value for q_8 comes out to be 17·6 mc./sec., in good agreement with the value of 17·8 mc./sec. that one gets in a similar manner from the lines in the transition $J = 1 \rightarrow 2$.

In order to calculate the frequencies of the spectral lines according to the above expressions, we need to know the parameters B_v, D_{JK} and

$$\frac{q_8^2}{[4\{(1-\zeta)A_v - B_v\}]}.$$

Of these B_v can be accurately calculated to be 9226·1 mc./sec. from the position of the line $J = 0 \rightarrow 1$ with $v_8 = 1$ for which transition *l*-type doubling is absent. The value $D_{JK} = 0{\cdot}16$ mc./sec.,

$$\frac{q_8^2}{[4\{(1-\zeta_8)A_v - B_v\}]} = 0{\cdot}15 \text{ mc./sec.}$$

and $D_J \simeq 0$ appear to give the best fit with the experimental data. The calculated and observed frequencies of the lines corresponding to the transitions $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ with $v_8 = 1$ are given in Table II. Substituting the above values of q_8 and B_v along with a value of

A_v ($\simeq A_0$) = 5·28 cm.$^{-1}$ obtained from the structure of the molecule known from microwave spectra[5] in the expression

$$\frac{q_8^2}{4\{(1-\zeta_8)A_v - B_v\}} = 0{\cdot}15,$$

ζ_8 comes out to be 0·94. This value of ζ_8 represents exactly the average of the value obtained by Venkateswarlu[1,2] and that obtained by Parker *et al.*[13] from their respective infra-red spectral data. If the values ω_8 = 361 cm.$^{-1}$[1,2] and $B_e \simeq B_0$ = 9198·8 mc./sec. are taken, the coefficient *a* comes out to be 1·13.

TABLE II

Frequencies and assignments for the rotational transitions $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ of CH_3CN with $v_8 = 1$

J	Assignment K	Assignment *l*	Observed frequency in mc.	Calculated frequency in mc.
1 → 2	±1	±1	36,942·15	36,940·35
			36,870·94	36,869·57
	0	±1	36,903·40	36,903·50
	±1	∓1		36,902·56
2 → 3	±1	±1	55,412·5	55,410·50
			55,307·0	55,304·34
	±2	±1	55,359·5	55,359·97
	0	±1	55,353·0	55,353·00
	±1	∓1		55,352·73
	±2	∓1	55,344·9	55,349·15

APPLICATION TO THE SPECTRA OF CH_3NC, CH_3CCH AND CF_3CCH

A look in the earlier data on similar transitions in the excited states of CH_3NC, CH_3CCH and CF_3CCH shows that the spectral patterns obtained are in general qualitative agreement with the Nielsen's theory, but, in all these cases there are inconsistencies similar to those mentioned above for CH_3CN.

It is felt that it would be worthwhile to go into these cases in detail and try to remove the inconsistencies in the values of the different parameters.

CH_3NC.—The spectrum obtained for CH_3NC by Kessler *et al.*[5] for the transition $J = 1 \rightarrow 2$ with $v_8 = 1$ shows two lines widely separated by 111·1 mc./sec. with a close doublet in between. The pattern observed is in good qualitative agreement with Nielsen's theory, but the values $D_{JK} = -0{\cdot}9$ mc./sec. and $\zeta_8 = -0{\cdot}16$ obtained by Nielsen[11] are improbable. This is because D_{JK} for the ground state is known[5] to be 0·22 mc./sec. and ζ_8 is known from infra-red spectral data to be positive and high. Thompson and Williams[3] obtained 0·92 and later Williams[17] obtained 0·94 for ζ_8 from their infra-red data.

It is found that these inconsistencies can be removed and at the same time a good agreement between the observed and the calculated positions of the spectral lines could be obtained if the following parameters are used:

$B_v = 10091{\cdot}86$ mc./sec., $D_{JK} = 0{\cdot}27$ mc./sec., $D \simeq 0$ and

$$\frac{q_8^2}{4\{(1-\zeta)A_v - B_v\}} = 0{\cdot}2 \text{ mc./sec.}$$

The separation of 111·1 mc./sec. between the two extreme lines gives the value 27·78 mc./sec. for q_8. The frequencies calculated using these constants and those observed by Kessler *et al.*[5] are shown in Table III.

TABLE III

Frequencies and assignments for the rotational transitions $J = 1 \rightarrow 2$ with $v_8 = 1$ in CH_3NC

Assignment K	Assignment l	Observed frequency in mc.	Calculated frequency in mc.
± 1	± 1	40,424·49 40,313·37	40,424·49 40,313·37
0	± 1	40,366·55	40,366·24
± 1	∓ 1	40,364·07	40,364·35

Substituting these values of q_8 and B_v along with A_v taken as $A_0 = 5{\cdot}36$ cm.$^{-1}$ which is evaluated from the known structure[5] of the molecule, in the expression

$$\frac{q_8^2}{4\{(1-\zeta)A_v - B_v\}} = 0{\cdot}2,$$

one gets $\zeta_8 = 0{\cdot}93$. This value of ζ_8 is just the mean of those obtained by Thomson and Williams[8] and Williams.[17] Using the value of $B_e \simeq B_0$ and $\omega_8 = 263$ cm.$^{-1}$[17] one can get the value for a as 1·08.

CH_3CCH.—Trambarulo and Gordy[18] applied the Nielsen's theory to identify the rotational spectra of CH_3CCH which they observed for the transitions $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ in the vibrational state for which v_{10} (C − C ≡ C bending) = 1. Their assignments give a value of 1·1 for ζ_{10} which is unlikely because this is not in agreement with that obtained recently by Rao and Palik[19] from infra-red spectral data and also because the maximum value that ζ can have is 1·00. Using the value of 1·1 for ζ_{10} one gets $\Delta\nu = -1{\cdot}6$ cm.$^{-1}$ for the average separation of the individual Q branches in the fundamental ν_{10}. The minus sign indicates[14] that ^RQ branches will be on the low frequency side of the origin and ^PQ branches will be high frequency side of the origin, while reverse would be the case if $\Delta\nu$ comes out to be positive. Rao and Palik[19] resolved the fundamental ν_{10} and found that the average separation between the Q branches comes to about 0·58 cm.$^{-1}$ and not 1·6 cm.$^{-1}$ This value of 0·58 cm.$^{-1}$ can of course be taken as positive or negative. If it is taken to be positive ζ_{10} comes out to be 0·89, and if it is taken to be negative, ζ_{10} comes out to be 1·00. The microwave spectral data cannot be explained if ζ_{10} is taken as 0·89. Therefore it appears that ^RQ branches fall on the low frequency side and ^PQ branches fall on the high frequency side of the origin in the fundamental ν_{10}, and ζ_{10} is to be taken as 1·00. Trambarulo and Gordy[18] also observed six lines for the transition $J = 2 \rightarrow 3$ in the excited C ≡ C − H bending vibrational state $v_9 = 1$. They stated that though the grouping of the lines agrees qualitatively with Nielsen's theory, no reasonable assignment of these lines could be made.

Using $\zeta_{10} = 1{\cdot}00$ and $q_{10} = 16{\cdot}76$ mc./sec. obtained from the widely separated lines,

$$\frac{q_{10}^2}{[4\{(1-\zeta_{10})A_v - B_v\}]}$$

comes out to be − 8 kc./sec. The frequencies of the spectral lines are calculated taking the above parameters along with the rotational constants $B_v = 8569{\cdot}75$, $D_{JK} = 0{\cdot}17$ mc./sec. and $D_J \simeq 0$ and are given in Table IV with the corresponding assignments. It is to be noted that the present assignments for the lines corresponding to the transition $J = 2 \rightarrow 3$ are different from those given by Trambarulo and Gordy,[18] but they are same for the li nes of the transition $J = 1 \rightarrow 2$.

TABLE IV

Frequencies and assignments for the transitions $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ of CH_3CCH for the excited bending $C-C\equiv C$ vibration $v_{10} = 1$

J	Assignment K	Assignment l	Observed frequency in mc.	Calculated frequency in mc.
$1 \rightarrow 2$	± 1	± 1	34,313·21	34,313·20
			34,246·30	34,246·16
	0	± 1	34,278·98	34,279·05
	± 1	∓ 1	34,277·05	34,276·96
$2 \rightarrow 3$	± 1	± 1	51,469·85	51,469·80
			51,369·12	51,369·24
	0	± 1	51,418·75	51,418·69
	± 2	± 1	51,418·23	51,418·31
	± 1	∓ 1	51,415·35	51,415·50
	± 2	∓ 1	51,410·51	51,410·44

The spectral lines corresponding to the transition $J = 2 \rightarrow 3$ in the excited vibrational state $v_9 = 1$ are identified as shown in Table V using the following parameters.

$B_v = 8551 \cdot 1$ mc./sec., $D_{JK} = 0 \cdot 17$ mc./sec., $D_J \simeq 0$,

$q_9 = 9 \cdot 06$ mc./sec. and

$$\frac{\left(\frac{3}{2} q_9^2\right)}{[(1 - \zeta_9) A_v - B_v]} = -0 \cdot 2 \text{ mc./sec.}$$

The value for ζ_9 is determined, in the same manner as stated earlier, as 0·95. Thus the sum of $\zeta_{10} + \zeta_9$ comes to be 1·95 which is in close agreement with that given by Boyd and Thompson[20] as 1·96.

Using the values for $\omega_{10} = 328 \cdot 0$ cm.$^{-1}$ and $\omega_9 = 633$ cm.$^{-1}$ given by Boyd and Thompson[20] the coefficient a in the bending vibrational mode

$C - C \equiv C$ and that in the mode $C \equiv C - H$ come out to be 1·14 and 1·19 respectively.

TABLE V

Frequencies and assignments for the transitions $J = 2 \rightarrow 3$ of CH_3CCH for the excited bending $C \equiv C-H$ vibration $v_9 = 1$

J	Assignment K	Assignment l	Observed frequency in mc.	Calculated frequency in mc.
$2 \rightarrow 3$	± 1	± 1	51,334·81	51,334·80
			51,280·45	51,280·44
	0	± 1	51,307·53	51,307·50
	± 2	± 1	51,305·93	51,305·70
	± 1	∓ 1	51,304·05	51,303·99
	± 2	∓ 1	51,296·33	51,298·74

CF_3CCH.—In computing the frequencies from Nielsen's theory Anderson *et al.*[16] used the values for ζ_{10} and

$$\frac{q_{10}^2}{[4\{(1-\zeta_{10})A_v - B_v)]}$$

as 1·5 and 7 kc./sec. respectively, which seem to be unlikely due to two reasons: (1) if ζ_{10} is taken 1·5, the value for

$$\frac{q_{10}^2}{[4\{(1-\zeta_{10})A_v - B_v\}]}$$

comes to be about $-0{\cdot}6$ kc./sec. and not 7·0 kc./sec. as taken by them, and (2) a value of 1·5 for ζ_{10} is improbable as ζ cannot be greater than 1.

These inconsistencies can be removed and all the observed lines in the excited bending vibration can be interpreted on the basis of Nielsen's theory, if the following parameters are used:

$B_v = 2883{\cdot}47$ mc./sec., $D_{JK} = 8$ kc./sec., $D_J = 0{\cdot}3$ kc./sec.,

$q_{10} = 3{\cdot}6125$ mc./sec. and

$$\frac{q_{10}^2}{[4\{(1-\zeta_{10})A_v - B_v\}]} = -6{\cdot}5 \text{ kc./sec.}$$

TABLE VI

Frequencies and assignments for the $J = 3 \rightarrow 4$, $J = 4 \rightarrow 5$ and $J = 8 \rightarrow 9$ rotational transitions of CF_3CCH with $v_{10} = 1$

J	Assignment K	Assignment *l*	Observed frequency in mc.	Calculated frequency in mc.
$3 \rightarrow 4^a$	± 1	± 1	23,082·4 23,053·5	23,082·43 23,053·45
	0	± 1		23,068·31
	± 1	∓ 1		23,067·93
	± 2	∓ 1	23,067·7	23,067·56
	± 3	± 1		23,067·44
	± 2	± 1		23,067·36
	± 3	∓ 1		23,067·09
$4 \rightarrow 5^b$	± 1	± 1	28,852·61 28,816·48	28,852·64 28,816·42
	0	± 1	28,835·26	28,835·29
	± 1	∓ 1	28,834·45	28,834·67
	± 2	∓ 1	28,834·20	28,834·16
	± 3	± 1	28,833·81	28,833·76
	± 2	± 1		28,833·62
	± 3	∓ 1		28,833·55
	± 4	± 1	28,833·22	28,833·46
	± 4	∓ 1	28,832[c]	28,832·82
$8 \rightarrow 9^b$	± 1	± 1	51,934·48 51,869·14	51,934·38 51,869·20

TABLE VI—*Contd.*

J	Assignment K	Assignment *l*	Observed frequency in mc.	Calculated frequency in mc.
	0	±1	51,906·64	51,906·43
	±1	∓1	51,903·42	51,903·67
	±2	∓1		51,902·20
	±4	±1	51,901·68	51,901·58
	±3	∓1	51,899·99	51,900·84
	±4	∓1	51,899·44	51,899·37
	±3	±1	51,898·61	51,898·76
	±5	±1		51,898·12
	±5	∓1	51,897·63	51,897·67
	±6	±1		51,897·03
	±2	±1	51,896·86	51,896·87
	±6	∓1		51,895·71
	±7	±1	51,894·95	51,895·55
	±7	∓1		51,893·52
	±8	±1	51,892·88	51,892·85
	±8	∓1	51,890·62	51,891·05

[a] Shoolery, Shulman, Sheehan, Schomaker and Yost, *J. Chem. Phys.*, 1951, **19**, 1364.

[b] *See* Reference 16.

[c] This frequency is measured with an accuracy of ± 1 mc. and the others are accurate to ± 0·20 mc.

Table VI shows the frequencies of the observed spectral lines along with those calculated using the above parameters. It is to be noted that the present assignments shown in the table differ from those given by Anderson *et al.*[16] for the transitions $J = 4 \rightarrow 5$ and $J = 8 \rightarrow 9$.

The value for ζ_{10}, as determined in the same manner as for the other molecules, is found to be 0·6. As no infra-red spectral data are available at present to check the correctness of this value of ζ_{10}, the parameters used here for CF_3CCH are to be treated to some extent as tentative.

Looking at the tables one can find that in the molecule CH_3CN, the deviations between the calculated positions of the lines from observed ones are somewhat more appreciable than those in other molecules dealt in this paper. These deviations might be because of the probable and appreciable effect of the nuclear quadrupole coupling constant of the nitrogen atom in CH_3CN. In methyl cyanide the quadrupole coupling constant for nitrogen is known[5] to be $-$ 4·35 mc./sec. whereas it is only | 0·5 | mc./sec. in CH_3NC and there is no atom in CH_3CCH or CF_3CCH having quadrupole coupling constant.

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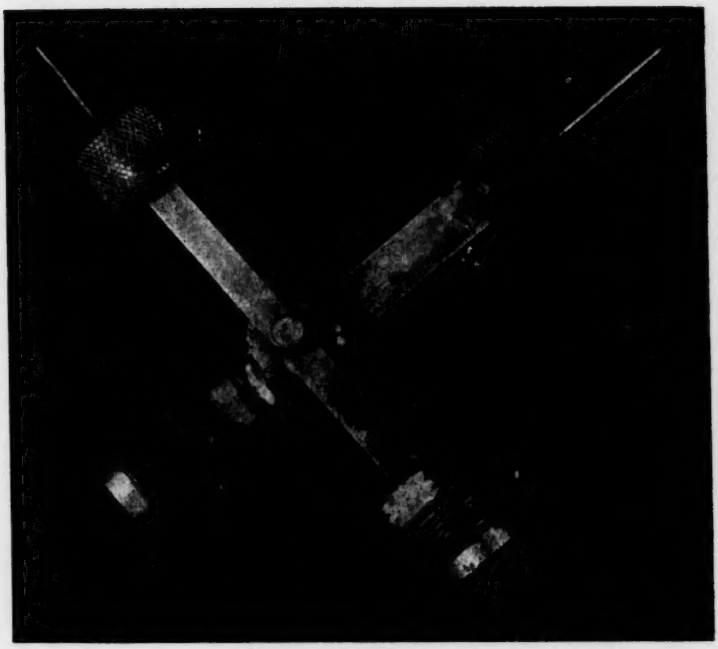

FIG. 1. J → I Multiplier

THE PHOTOLYTIC SEPARATION OF URANIUM FROM ALUMINIUM AND THORIUM, CERIUM AND LANTHANUM

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The photolytic process of isolation of the hydrated uranium complex[1] NH_4F, UF_4, H_2O has been applied for the separation of uranium from aluminium and from a mixture of thorium, cerium and lanthanum. The waste products of reactor contain about 95 per cent. of unconsumed uranium along with aluminium from which the former is separated by solvent extraction process.[2] A convenient photochemical method for bringing about the separation has been achieved by us. When ammonium bifluoride is added to an aqueous solution of the nitrates of uranium and aluminium, a considerable portion of the latter, if present in large excess, is precipitated as fluoride which is filtered off. The filtrate with 10 per cent. of alcohol on exposure to sunlight undergoes photolysis and uranium is precipitated in the form of the hydrated fluoride complex. By single exposure 99 per cent. of uranium of 100 per cent. purity is obtained as shown in Table I.

TABLE I

Composition of the mixture of nitrates calculated as oxides		Estimation of the uranium precipitate calculated as U_3O_8		Percentage of recovery
U_3O_8 mg.	Al_2O_3 mg.	On ignition mg.	By Jones reductor mg.	
522·5	592·5	519·0	519·0	99·3
522·5	592·5	517·0	518·2	98·9
250·8	151·5	249·0	248·7	99·3
250·8	151·5	248·8	249·0	99·2
250·8	75·7	248·8	248·7	99·2
250·8	75·7	249·2	249·0	99·4

The same photolytic process has been applied for the separation of uranium from thorium, cerium and lanthanum. In place of ammonium fluoride used by Krishnaprasad and Dadape,[3] ammonium bifluoride has been used by us, as it has the advantage of automatically fixing up the pH at about 4·7 suitable for the precipitation of the complex fluorides of thorium, cerium and lanthanum, leaving the uranium in the solution. After filtering off the insoluble fluoride, the solution of the nitrates is exposed to sunlight with 10 per cent. of alcohol when uranium is precipitated in the form of the hydrated complex mentioned above. Only with single exposure for four hours, as can be seen from the data recorded in Table II, 93–95 per cent. of uranium initially taken is recovered in the pure state.

The recovery of uranium has been estimated from the U_3O_8 content of an aliquot part of the solution of the residue in nitric acid. For the estimation of percentage of purity, another aliquot part of the solution was heated with sulphuric acid after which uranium content was estimated by Jones reductor method.[4]

TABLE II

Composition of the mixture of the nitrates calculated as oxides				Estimation of the uranium precipitate calculated as U_3O_8		Percentage of recovery
U_3O_8 mg.	ThO_2 mg.	CeO_2 mg.	La_2O_3 mg.	On ignition mg.	By Jones reductor method mg.	
472·5	126·0	111·2	156·8	447·8	448·2	94·8
472·5	126·0	111·2	156·8	438·8	436·2	92·9
472·5	126·0	111·2	156·8	452·0	451·0	95·5
472·5	126·0	111·2	156·8	450·0	449·6	95·2

The photolytic separation of uranium from vanadium and iron will be the subject-matter of our next communication.

SUMMARY

The separation of uranium from aluminium and thorium, cerium and lanthanum has been accomplished by photochemical process. Sunlight has been used as the source of energy for the photolysis. No loss of uranium

occurs as the solution containing the remaining quantity of uranium which is not precipitated can be used again. By this photolytic process 100 per cent. pure uranium is obtained. The recovery is 99 per cent. when the separation is made from aluminium and 93–95 per cent. when it is made from the mixture with thorium, cerium and lanthanum.

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THE PROBLEM OF THE COMPOSITION AND STRUCTURE OF POTASSIUM CYANO-COBALTATE (II)

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Introduction

The question regarding the composition and structure of the compound formed by the addition of excess of KCN to Co (II) still remains in a controversial state in spite of the large amount of work done on this problem. This paper describes our attempt in this direction, using potentiometric and polarographic methods.

The preparation and properties of potassium cyanocobaltate (II) have been described by Descamp,[1] Manchot and Herzog[2] and Grube.[3] Grube obtained the complex by the electrolytic reduction of potassium cyanocobaltate (III) in alkaline medium and gave its oxidation potential as 0·821 volt for a Co (III)/Co (II) ratio of 0·086 : 0·014 mole.

A large number of workers have studied the molecular formula of the compound. Amongst these workers mention may be made of Szego and Ostinelli,[4] Sartori,[5] Peters,[6] Lowry[7] and Emelianova[8] whose investigations led to the formulation $K_4Co(CN)_6$; whereas evidences for the formation of a pentacyanide were obtained from the work of Monval and Paris,[9] Rupp and Pfenning,[10] Edelman,[11] Muller and Schluttig[12] and Glastone and Speckman.[13]

In recent years investigations on this complex using potentiometric, polarographic and radiochemical methods have been carried out by Treadwell and Huber,[14] Iguchi,[15] Cremoux and Monval,[16] Hume and Kolthoff[17] and Adamson.[18] Adamson, on the basis of exchange studies, observed that there was no conclusive evidence for the existence of hexacyanocobaltate (II) and that the available information did not distinguish between the two likely structures for the pentacyanide in solution, namely, $[Co(CN)_5H_2O]^{3-}$ and $[Co(CN)_5]^{3-}$. Smith and co-workers[19] on the basis of titration curves and spectrophotometric data concluded that $[Co(CN)_4(OH)_2]^{3-}$ and $[Co(CN)_6]^{3-}$ are formed in the early stages of oxidation of the compound.

Experimental

The method recommended by Smith and co-workers[19] was followed for the preparation of the complex. The dried substance was then analysed for Co, K and CN, and the water content was determined by subtracting the total percent of the constituents from hundred.

Estimation of cobalt.—Cobalt was estimated volumetrically by potassium cobaltinitrite method.[20] The complex was broken by digesting with concentrated H_2SO_4 and this solution was also used for the estimation of K.

Estimation of potassium.—Potassium was estimated by cobaltinitrite method[21] and checked by colorimetric method using Lange's Flame Photometer. The results were found to be in good agreement.

Estimation of CN.—Kjeldahl's method combined with Colmann method as recommended by Smith, Kleinberg and Griswold,[19] with slight modifications, was followed for the estimation of CN.

From the percentage of the constituents, the empirical formula was calculated as below:

Constituent	Percentage	Equivalent	Ratio
Co	17·81	0·3021	1·0
K	36·66	0·9376	3·103
CN	40·05	1·5400	5·098
H_2O	5·48	0·3045	1·008

Hence the empirical formula may be written as $K_3Co(CN)_5 H_2O$ (+ 0·1 KCN) which means that the complex has got the composition $K_3Co(CN)_5 H_2O$ and it contains about 0·1 mole of KCN adsorbed per mole of the complex. This adsorption of KCN can be quite realised since the complex was precipitated from a solution containing excess of KCN.

The equivalent weight of the complex was determined as follows: 20·0 c.c. of 0·1 N $K_3Fe(CN)_6$ was mixed with 5·0 c.c. of 0·1 N KCN and an accurately weighed amount (0·3307 gm.) of the complex was added to it. The complex reduced the ferri- to ferrocyanide and the excess of ferricyanide was estimated by the method of Muller and Diefenthaler.[22] The equivalent weight then calculated was found to be 322·5 almost in agreement

with the empirical formula weight (324) calculated on the basis of analytical data.

The composition of the complex was also determined by carrying out amperometric and potentiometric titrations between cobalt nitrate and potassium cyanide solutions. Amperometric titrations were carried out at $2 \pm 0{\cdot}1°$ C. with KCl (0·5 M) as supporting electrolyte and gelatine (0·005%) as maximum suppressor, at a potential of $-1{\cdot}25$ volts (determined from the polarogram of cobalt nitrate solution, taken under identical conditions). Some of the readings for direct and reverse titrations are summarised in the following table and the curves are given in Fig. 1. A Fisher electropode with an external Multiflex-galvanometer (type MGF 2) was used for the experiments.

Vol. of Co (II) soln.	Conc. of Co (II) soln.	Vol. of KCN soln.	Strength of KCN	Ratio Co (II): KCN
	(*a*) Direct titrations [Co (II) in the cell]			
25 c.c.	0·010 M	2·55 c.c.	0·5 M	1 : 5
25 c.c.	0·005 M	1·25 c.c.	0·5 M	1 : 5
	(*b*) Reverse titrations (KCN in the cell)			
1·0 c.c.	0·1 M	25 c.c.	0·02 M	1 : 5
2·1 c.c.	0·1 M	25 c.c.	0·04 M	1 : 5

In the case of direct titrations, two breaks were obtained (*vide* Fig. 1 *a*) after the addition of 2 and 5 equivalents of KCN respectively.

Potentiometric titrations also gave two breaks (*vide* Fig. 2), the first appearing due to the formation of $Co(CN)_2$. The results for the second break are summarised below:

Strength of Co (II) soln.	Vol. of Co (II) soln.	Strength of KCN soln.	Vol. of KCN in the same molar conc.	Probable ratio
0·01 M	25 c.c.	0·5 M	127·3 c.c.	1 : 5
0·02 M	25 c.c.	0·5 M	126·3 c.c.	1 : 5
0·01 M	25 c.c.	0·25 M	127·5 c.c.	1 : 5
0·02 M	25 c.c.	0·25 M	126·9 c.c.	1 : 5

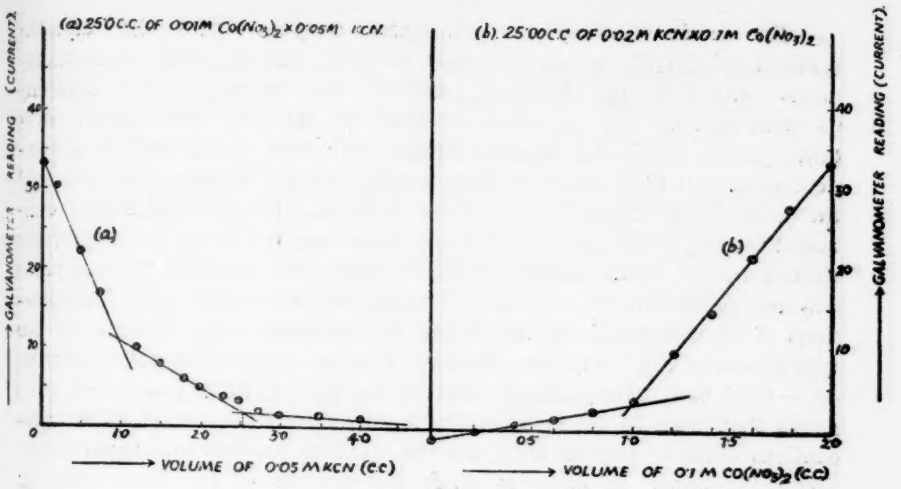
(a) 25·0 C.C. OF 0·01M $Co(No_3)_2$ × 0·05M KCN
(b) 25·00 C.C. OF 0·02M KCN X0·1M $Co(No_3)_2$
GALVANOMETER READING (CURRENT)
(a)
(b)
VOLUME OF 0·05M KCN (C.C)
VOLUME OF 0·1M $Co(NO_3)_2$ (C.C)

FIG. 1. Amperometric titrations.

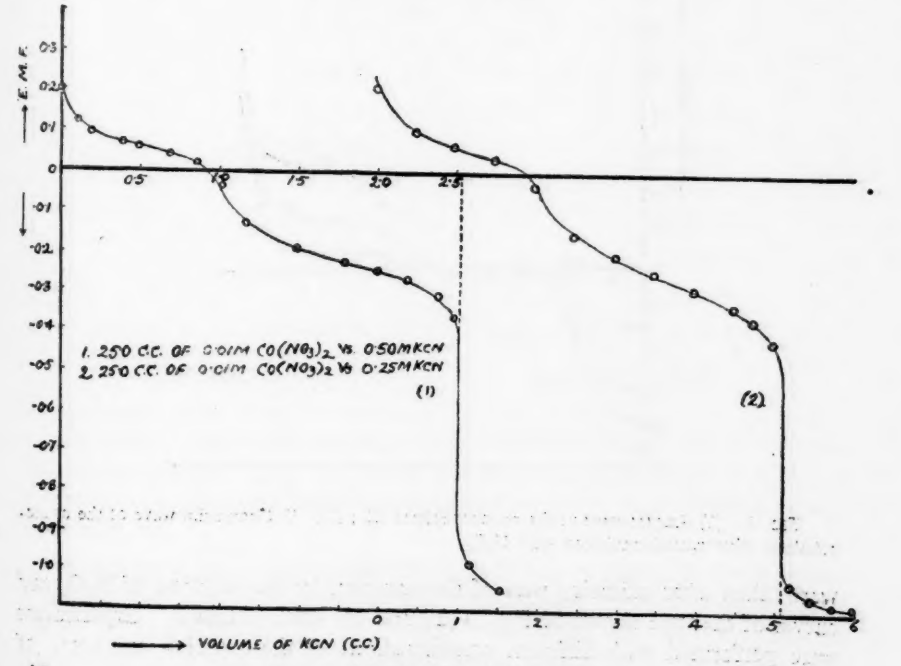

FIG. 2. Potentiometric titration curves.

The anodic wave of the pentacyano complex.—Since the aqueous solution of Co (II) complex is very unstable and is liable to instantaneous oxidation, the following method was employed for studying its polarogram. The solutions obtained in the cell after direct titrations [taking $Co(NO_3)_2$ solution in the cell] were maintained at a temperature $2 \pm 0{\cdot}1°$ C. under an inert atmosphere (of nitrogen gas) and used for the study of the polarogram of the complex. The solution already contained 0·005% gelatin as maximum suppressor and 0·5 M KCl as supporting electrolyte. (A small quantity of KCN added after reaching the end-point was also present in the solution.) Polarograms were taken with concentrations of the complex 5, 10, 20, 30 and 50 millimoles/litre. Curves of the type shown in Fig. 3 (1) were obtained, with the anodic half-wave potential of $-0{\cdot}35$ volt. The cathodic part of the wave (with $E\frac{1}{2} = -1{\cdot}3$ volt) shows that some of the solution had been oxidised (in spite of all the precautions taken to prevent that) and this oxidised product undergoes reduction at the d.m.e. In order to verify this portion of the wave, readings

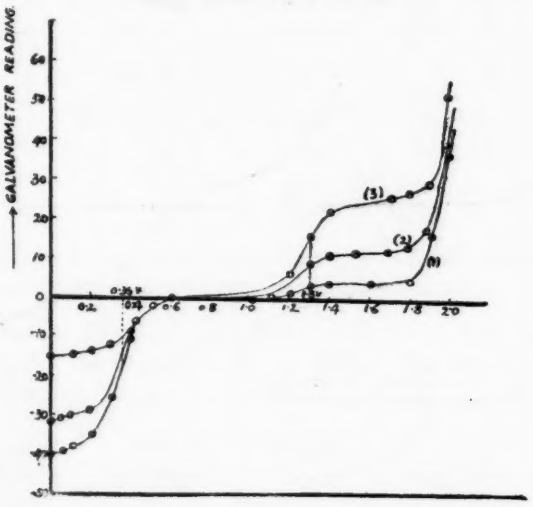

FIG. 3. (1) Anodic wave of the cyanocobaltate (II); (2), (3) Composite wave of the cyanocobaltate after partial oxidation with H_2O_2.

were taken after oxidising part of the complex by the addition of H_2O_2 and curves of the type shown in Fig. 3 (2) and (3) were obtained. Experiments were performed with different concentrations of the complex and some of the readings are given in Tables I and II.

TABLE I

Readings for the anodic wave of the cyano-complex

Pot. *vs.* S.C.E. in volts	Galv. readings in mm.
0·0	−40·0
0·05	−39·0
0·1	−37·5
0·2	−34·5
0·3	−25·0
0·4	−10·0
0·5	− 2·5
0·6	− 0·5
1·0	0·0
1·1	+ 0·5
1·2	+ 1·5
1·3	+ 3·5
1·4	+ 4·5
1·7	+ 4·5
1·8	+ 5·0
1·9	+16·0
2·0	+36·0

[*vide* Fig. 3—(1)]

TABLE II

Readings for the composite wave of the complex after partial oxidation with hydrogen peroxide

Pot. *vs.* S.C.E. in volts	Galv. readings in mm.
0·0	−15·0
0·05	−14·5
0·1	−14·5
0·2	−13·5
0·3	−12·0
0·4	− 8·0
0·5	− 2·0
0·6	− 0·5
1·0	+ 1·5
1·1	+ 2·0
1·2	+ 6·0
1·3	+16·5
1·4	+22·5
1·7	+22·5
1·8	+26·5
1·9	+29·0
2·0	+52·0

[*vide* Fig. 3—(2)]

In order to study the identity of this oxidised product and of hydroxo-pentacyanocobaltate (III), the latter was prepared by the method followed by Smith and co-workers[19] and its polarogram was taken under identical conditions (Fig. 4).

From the curves it is seen that by the addition of H_2O_2, the pentacyano-cobaltate (II) undergoes oxidation and the oxidised product is reducible at the d.m.e. at a potential of − 1·3 volts. Both these electrode reactions are irreversible as is seen from the nature of the curves, *i.e.*, a large influxion

at zero current and the great difference between the anodic and cathodic half-wave potentials.

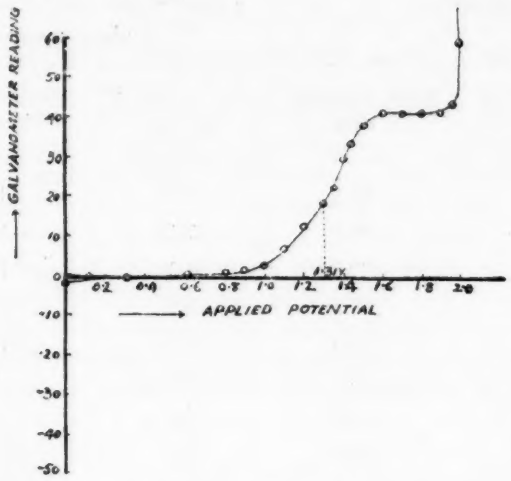

FIG. 4. Polarogram of the hydroxocompound [Hydroxopenta-cyanocobaltate (III)].

DISCUSSION

The results on chemical analysis, amperometry and potentiometry of the complex lead to interesting conclusions regarding its composition and structure. Not only ample evidence is available to show that five molecules of potassium cyanide react with one mole of Co (II), but some insight into the problem whether the complex is penta- or hexa- co-ordinated, has been achieved. No doubt that the method of chemical analysis fails to provide a clear answer to the structural complexity of the compound, yet it can be seen that the product formed by the interaction of KCN and Co (II) has got the empirical formula $K_3Co(CN)_5H_2O$ (with about 0·1 KCN adsorbed per mole). The equivalent weight of the compound was found to be 322·5 which closely agrees with the value calculated for $K_3Co(CN)_5H_2O$. The potentiometric and amperometric titrations also show that the complex is a pentacyanide but no information regarding its co-ordination (penta or hexa) is obtained from these methods.

The polarographic studies also give results of considerable value. It has been found that the freshly prepared complex gives a clear anodic wave with $E_{\frac{1}{2}} - 0{\cdot}35$ volt. This wave cannot be merely due to the small amount of KCN present in the solution since it is suppressed to a great extent on

oxidising the complex with H_2O_2. From this fact it can be safely concluded that the presence of the pentacyanocobaltate (II) contributes mostly for the appearance of the anodic wave. It is worthwhile to mention that Hume and Kolthoff could not get an anodic wave for the complex since they studied the polarogram in 1 M KCN at the potential of $-0{\cdot}8$ volt and onward.

A better insight into the structure of the complex is obtained from the fact that the oxidised product (*vide supra*) is irreversibly reduced at the d.m.e. at a potential of $-1{\cdot}3$ volts (*vide* Fig. 3). A similar polarogram was obtained by us for the hydroxocompound prepared by the method of Smith and co-workers, again with $E\frac{1}{2} - 1{\cdot}3$ volts. This goes to prove that the product is hydroxopentacyanocobaltate (III). Moreover a cathodic wave either with KCN or KCl as supporting electrolyte was not observed for the hexacyanide obtained by boiling the hydroxocompound. From these observations it is evident that the original product formed by the addition of KCN to $Co(NO_3)_2$ is $K_3[Co(CN)_5H_2O]$ which is oxidised in solution to $K_3[Co(CN)_5OH]$ and not $K_3[Co(CN)_6]$.

Further confirmation could be obtained when the product in the air-tight cell obtained after the potentiometric titration was immediately oxidised with a few c.c. of H_2O_2 and titrated against $0{\cdot}1$ N HCl (using a Beckman pH meter with glass and calomel electrodes). Two distinct breaks, in agreement with the observations of Smith and co-workers, were obtained. Their assumption that the hydroxocomplex undergoes a change:

$$2K_3[Co(CN)_5OH] \rightarrow K_3[Co(CN)_4(OH)_2] + K_3[Co(CN)_6]$$

incidentally finds support by these experiments.

To account for the instability of Co (II) cyanide complex, Pauling[23] suggested that in order to free two *d* orbitals for complex formation, the seventh *d* electron in the cobalt (II) ion is promoted to a higher energy level where it is easily lost to give the Co (III) complex. This explanation has been criticised on the following grounds. Firstly because the hydrated Co (III) ion is also diamagnetic and thus it should have a little tendency to pick up an unshared electron in the excited level and change over to Co (II). But this change is contrary to experimental facts. Secondly, Adamson (*loc. cit.*) on the basis of exchange reactions with radiocyanide has given $K_3Co(CN)_5$ as the formula of the complex. This formula involves a co-ordination number five with $3d^1\,4s^1\,4p^3$ hybridisation, which at the same time eliminates the necessity for the promotion of the electron to higher energy level.

The existence of cobalt cyanide complex with a co-ordination number five is not also theoretically sound. This number is the least likely to exist

in a compound with such strongly bound CN groups. Complexes showing such abnormal co-ordination number not only differ in the nature of linkages but also have been found to exist as tetra-co-ordinated and hexa-co-ordinated ions.[24–29] Amongst these include IF_5; PBr_5; $PCl_5(CH_3)_3SbCl_2$; Cs_3CoCl_5, etc. Kimball[30] gave trigonal pyramid, tetragonal pyramid, pentagonal plane and pentagonal pyramid configurations for these compounds. On the basis of Pauling's original theory, a planar configuration is most likely for ions having one *d* orbital available for bond formation. Moreover, compounds in which the central atoms appear to be five co-ordinated in solid state, dissociation takes place in solution. For example, Cs_3CoCl_5 has been shown to be made up of tetrahedral tetrachlorocobaltate (II) ion and Cs^+ and Cl^- ions.[31]

The magnetic behaviour of the complex is also baffling. The solid has been reported to be diamagnetic,[4] while it actually should show paramagnetism. On the other hand, the solution is paramagentic showing that it contains unpaired electron. Equally interesting is the behaviour in the case of Co (III) complexes which show $3d^2\,4s^1\,4p^3$ hybridisation and should be diamagnetic. That this is not the case has been demonstrated by Cambi, Ferrari and Nardelli[32] for a number of hexanitrocobaltate (II) complexes. The appreciable paramagnetism of these compounds suggests contribution from incompletely quenched orbitals although for ions of transitional elements, orbital angular momentum should be negligible. From the above, it is thus evident that magnetic measurements fail to give an idea concerning orbital hybridisation, degree of covalent character and probable structure for a large majority of cobalt complexes, including of course, cyanogen complexes.

Our experimental results on the physico-chemical investigations on Co (II) cyanide complex definitely show that five CN radicals are bound to the central atom and further suggest that the co-ordination number six is maintained by co-ordinating with a water molecule. This behaviour can be explained if we assume that pairing of odd electrons in Co (II) occurs by dimer formation, through a water bridge as $(CN)_5Co\overset{\equiv}{\underset{H}{\overset{H}{—O—}}}Co(CN)_5\overset{\equiv}{\cdot}H_2O$, the second H_2O being lattice bound. Similar explanation has been put forward for silver pentacyanocobaltate (III) which in the hydrated form was diamagnetic.

From the above consideration it may, therefore, be concluded that the cyanocobaltate (II) exists in a hexacovalent state both as a solid and in solu-

tion. In the solid form, the aquopentacyanocobaltate (II) is stable only when air and moisture are excluded, but it is readily converted to the hexa-co-ordinated hydroxopentacyanocobaltate (III) when brought in solution. The latter product undergoes a gradual change—

$$2\,K_3[Co(CN)_5OH] \rightarrow K_3[Co(CN)_4(OH)_2] + K_3[Co(CN)_6]$$

On prolonged standing or on boiling, the hexacyanocobaltate (III) is the final product of oxidation.

Thanks are due to Prof. M. O. Farooq for his keen interest in the progress of this work.

Summary

An approach to the problem of the composition and structure of potassium cyanocobaltate (II) has been made. The complex prepared by the interaction of Co (II) and KCN gave, on analysis, a compound with the formula $K_3Co(CN)_4H_2O$ (with about 0·1 M KCN adsorbed per mole). Potentiometric and amperometric titrations carried out between cobalt (II) nitrate and potassium cyanide gave support to the formation of a pentacyanocobaltate (II) but failed to give an insight into the structure of the complex. Polarographic studies, however, were found useful in deciding whether the complex is hexa- or penta-co-ordinated. The freshly prepared complex gave an anodic wave with $E_{\frac{1}{2}} - 0{\cdot}35$ volt. This is due to pentacyanocobaltate (II), since the anodic wave is suppressed and finally eliminated by oxidising the compound with H_2O_2. The oxidised product was found to be irreversibly reduced at the dropping mercury electrode (d.m.e.) at a potential of $-1{\cdot}3$ volts. That the product is hydroxopentacyano-cobaltate (III) could be seen by getting identical polarograms for the oxidised product and for a sample of the hydroxocompound. From these experiments it has been concluded that the original complex is a hexaco-ordinated compound with the formula $K_3[Co(CN)_4.H_2O]$ and it gets oxidised to $K_3[Co(CN)_5OH]$ $K_3[Co(CN)_5.OH]$ and finally to $K_3[Co(CN)_4]$ on long standing or on boiling. It appears that either five cyanogen radicals are bound to the central atom and the co-ordination number six is maintained by co-ordinating with a water molecule, or a dimer through a water bridge as

$$(CN)_5Co\overset{\equiv}{\underset{}{}}\!-\!\underset{H}{\overset{H}{O}}\!-\!\overset{\equiv}{\underset{}{}}Co(CN)_5\cdot H_2O \text{ is formed.}$$

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A GENERAL TRANSFORM—GAUSS TRANSFORM

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It is well known that the theory of orthogonal functions suggests a set of transforms (refer for instance, Sneddon, 1955). The author (1958) showed recently from certain general considerations that a polynomial defined by

$$p_n(x) = \frac{1}{K_n \omega(x)} \left(\frac{d}{dx}\right)^n [(ax^2 + bx + c)^n \cdot \omega(x)] \tag{1}$$

where

$$\omega(x) = \exp - \int^x \frac{pt + q}{at^2 + bt + c}\, dt$$

a, b, c, p, q do not contain n, satisfies the second order differential equation

$$(ax^2 + bx + c)\frac{d^2y}{dx^2} + [(2a - p)x + b - q]\frac{dy}{dx}$$

$$+ n[p - (n + 1)a]y = 0 \tag{2}$$

and that $p_n(x)$ is an orthogonal polynomial in some interval (α, β). It was also shown that $p_n(x)$ unifies all the classical orthogonal polynomials for special values of a, b, c, p, q and it was christened " Gauss Polynomial".

In the present communication we define a new transform ' Gauss Transform '—so as to include all the classical orthogonal polynomial transforms such as " Jacobi Transforms " of Scott (1953), Tranter's (1950) " Legendre Transform ", " Gegenbauer Transform " of Lakshmana Rao (1954, 1956) and others like Hermite and Laguerre Transforms. We also develop two theorems of much practical use concerning this transform.

2. Let $f(x)$ be defined in a certain interval (α, β) where α, β are such that

$$\int_\alpha^\beta p_n(x)\, p_m(x)\, \omega(x)\, dx = \lambda_n \delta_{mn}; \tag{3}$$

and

$$\lambda_n = \frac{(-1)^n}{K_n} \int_\alpha^\beta (ax^2 + bx + c)^n \cdot \omega(x) \cdot \left[\left(\frac{d}{dx}\right)^n p_n(x)\right] dx.$$

We may then define either of the sequences of numbers

$$f_1(n) = T_1\{f(x)\} = \int_\alpha^\beta \omega(x).f(x).p_n(x)\,dx \tag{4}$$

and

$$f_2(n) = T_2\{f(x)\} = \int_\alpha^\beta f(x).p_n(x)\,dx \tag{5}$$

as the Gauss transforms of $f(x)$.

Let $f(x)$ defined as above in (α, β) be so conditioned that we may represent it in either of the forms

$$f(x) = \sum_{n=0}^{\infty} A_n p_n(x)$$

or

$$f(x) = \sum_{n=0}^{\infty} B_n \omega(x)\, p_n(x).$$

In view of (3) and definitions (4) and (5) we have the following formal expansions of $f(x)$:

$$f(x) = \sum_{n=0}^{\infty} \frac{f_1(n)}{\lambda_n} p_n(x) \tag{6}$$

$$f(x) = \sum_{n=0}^{\infty} \frac{f_2(n)}{\lambda_n} \omega(x)\, p_n(x). \tag{7}$$

3. THEOREM A.—Let $f''(x)$ be bounded and integrable in every closed subinterval of (α, β). Then if

$$\left.\begin{aligned} &(a)\ \operatorname*{Lt}_{x\to\alpha,\,\beta} (ax^2+bx+c).\omega(x).f(x) = 0 \\ &\quad\ \operatorname*{Lt}_{x\to\alpha,\,\beta} (ax^2+bx+c)\,\omega(x) f'(x) = 0 \end{aligned}\right\}$$

then

$$T_1\left\{\frac{1}{\omega(x)} \cdot \left(\frac{d}{dx}\right)[(ax^2+bx+c).\omega(x).f'(x)]\right\}$$
$$= -n\,[p-(n+1)\,a]\ f_1(n). \tag{8}$$

or if

$$(b)\ \left.\begin{aligned}&\underset{x\to\alpha,\,\beta}{\text{Lt}}\ (ax^2+bx+c)f(x)=0\\&\underset{x\to\alpha,\,\beta}{\text{Lt}}\ (ax^2+bx+c)f'(x)=0\end{aligned}\right\},$$

then

$$T_2\left\{\left(\frac{d}{dx}\right)[(ax^2+bx+c)f'(x)+(px+q)f(x)]\right\}$$

$$=(px+q)f(x)\,p_n(x)\Big|_\alpha^\beta - n\,[p-(n+1)\,a]\,f_2(n). \qquad (9)$$

Proof: Case (a).—

$$T_1\left\{\frac{1}{\omega(x)}\left(\frac{d}{dx}\right)\cdot[(ax^2+bx+c).\omega(x).f'(x)]\right\}$$

$$=\int_\alpha^\beta p_n(x)\cdot\left(\frac{d}{dx}\right)[(ax^2+bx+c)\,\omega(x)f'(x)]\,dx.$$

On integrating by parts twice and using the conditions on $f(x)$ and $f'(x)$ we get

$$T_1\left\{\frac{1}{\omega(x)}\cdot\left(\frac{d}{dx}\right)[(ax^2+bx+c)\,\omega(x)f'(x)]\right\}$$

$$=\int_\alpha^\beta f(x)\cdot\left(\frac{d}{dx}\right)[(ax^2+bx+c)\,\omega(x)\,p_n'(x)].dx.$$

Now using

$$\left(\frac{d}{dx}\right)[(ax^2+bx+c).\omega(x)\,p_n'(x)] = -\,n\,[p-(n+1)\,a]\,p_n(x)$$

we get the first result.

Case (b).—Here

$$T_2\left\{\left(\frac{d}{dx}\right)[(ax^2+bx+c)f'(x)+(px+q)f(x)]\right\}$$

$$=\int_\alpha^\beta p_n(x)\cdot\left(\frac{d}{dx}\right)[(ax^2+bx+c)f'(x)+(px+q)f(x)].dx.$$

This on integrating by parts and using the condition on $f'(x)$ becomes

$$= (px + q)\, p_n(x) f(x)\Big|_\alpha^\beta - \int_\alpha^\beta [(ax^2 + bx + c)\, p_n'(x).f'(x) + (px + q)\, p_n'(x) f(x)]\, dx.$$

Integrating by parts the first of the terms in the integrand again and using the condition on $f(x)$, we get

$$\mathrm{T}_2 \left\{\left(\frac{d}{dx}\right)[(ax^2 + bx + c) f'(x) + (px + q) f(x)]\right\}$$

$$= (px + q) f(x) \cdot p_n(x)\Big|_\alpha^\beta + \int_\alpha^\beta f(x) \left\{\left(\frac{d}{dx}\right) \times [(ax^2 + bx + c)\, p_n'(x)] - (px + q)\, p_n'(x)\right\} \cdot dx$$

Using (2), we arrive at the second result.

4. We may find the inverse of the first of the operational relations of Theorem (A). For let R denotes the differential operator

$$\mathrm{R} = \frac{1}{\omega(x)} \cdot \left(\frac{d}{dx}\right)\left[(ax^2 + bx + c) \cdot \omega(x) \cdot \left(\frac{d}{dx}\right)\right]. \tag{10}$$

If

$$\mathrm{R}[g(x)] = f(x) \tag{11}$$

and if $f(x)$ is a function of bounded variation on each interval $x \leq \xi \leq \alpha$, where α is the smaller of α, β; and that

$$\int_\alpha^\beta \omega(x) f(x)\, dx = 0 = f_1(0);$$

then the first integral of (11)

$$(ax^2 + bx + c)\, \omega(x)\, g'(x) = \int_\alpha^\beta \omega(\xi).f(\xi).d\xi$$

is a continuous function of x for $\alpha \leq x \leq \beta$ with limit zero as $x \to \beta$. Then the second integral

$$g(x) = \mathrm{R}^{-1}[f(x)]$$

$$= \int_0^\beta \frac{d\eta}{(a\eta^2 + b\eta + c)\, \omega(\eta)} \int_\alpha^\eta \omega(\xi) f(\xi)\, d\xi + \mathrm{C} \tag{12}$$

where C is an arbitrary integration constant, and is such that

$$(ax^2 + bx + c)\,\omega(x)\,g(x) \to 0 \quad \text{as } x \to \alpha, \beta.$$

The conditions of Theorem (A) expressed by the equations (8) are therefore satisfied, and hence $T_1\{R[g(x)]\}$ exists and that

$$T_1\{R[g(x)]\} = -n[p-(n+1)a]\,T_1\{g(x)\}$$

i.e.,

$$T_1\{f(x)\} = -n[p-(n+1)a]\,T_1\{R^{-1}[f(x)]\} \tag{13}$$

Hence we have

THEOREM B.—If $f(x)$ is a function of bounded variation in every closed subinterval (α, β) and

$$f_1(0) = \int_\alpha^\beta f(x)\,\omega(x)\,dx = 0,$$

then

$$T_1\{R^{-1}[f(x)]\} = -\frac{1}{n[p-(n+1)a]}\,T_1\{f(x)\}. \quad (n = 1, 2, \ldots)$$

and

$$T_1^{-1}\left\{\frac{-f_1(n)}{n[p-(n+1)a]}\right\} = R^{-1}[f(x)]$$

$$= \int_0^s \frac{ds}{(as^2+bs+c)\cdot\omega(s)} \int_\alpha^s \omega(t)\,f(t)\,dt + C$$

where C is a constant and determines

$$R^{-1}\{f(x)\}$$

when $n = 0$.

It may be mentioned here that the Hermite and Laguerre transforms, though do not appear to be formulated or widely used, may at once be defined with the help of the table in the author's article (1958) quoted above and the above two theorems A, B. It may also be mentioned that the Hermite transform (for which we put $a = b = q = 0$; $c = -1$, $p = -2$) may be used to solve the problem of simple harmonic oscillator in wave mechanics; and the Laguerre transform (for which we put $a = c = 0$, $b = p = 1$, $q = -\lambda$)

may be used to solve the Schrodinger's equation with the Morse potential, with considerable ease.

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THE DIPOLE MOMENTS AND MOLECULAR STRUCTURE OF PHENYLHYDRAZINE DERIVATIVES OF CARBONIC ACID

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Introduction

Hydrazine reacts in the same way as ammonia with carbonic acid, an example of this being its reaction with diethyl carbonate to give the ethyl ester of carbazic acid which in turn undergoes further solvolysis into carbohydrazide, the hydrazine analog of urea. Though dipole moment measurements have been reported for a number of substituted ureas[6–7] and acid hydrazides,[3, 8] no work appears to have been done on carbohydrazide derivatives. In view of this an investigation of the dipole moments of a few simple substituted derivatives of carbohydrazide was undertaken so as to ascertain whether the contribution of polar resonance forms is important in the structure of carbohydrazide and carbazone derivatives. The particular compounds studied are diphenyl carbohydrazide, diphenyl carbazone and diphenyl thiocarbazone in dioxan solutions.

Experimental

Materials.—Diphenyl carbohydrazide, a B.D.H. product, was twice recrystallised from ethyl alcohol, yielding pink needles, m.p. 170° C. Diphenyl carbazone, a B.D.H. product, was twice recrystallised from ethyl alcohol yielding orange red needles, m.p. 157° C. (decomp.). Diphenyl thiocarbazone was twice recrystallised from chloroform–ethyl alcohol mixture, to yield bluish black crystals. Commercial dioxan was purified by the Eigenberger's method, complete details of which have been given in an earlier paper.[11]

Apparatus and methods of measurement.—Measurements of dielectric constants were made using an A.C. mains-operated heterodyne beat apparatus similar to that of Hudson and Hobbs,[5] complete details of which have been given in an earlier paper.[11] Densities of the dilute dioxan solutions were obtained using an Ostwald-Sprengel pycnometer with closed ground in caps at both ends. Dipole moments were calculated by the modified Hedestrand's

method[4] similar to that introduced by Halverstadt and Kumler[3] differing only in that densities were used instead of specific volumes. Atomic polarisation was neglected and the molar refractions were calculated from the bond refractions of Denbigh.[2]

TABLE I

Temperature 35° ± 0·01° *C.*

Mole fraction	Dielectric constant	Density
	Symm. diphenyl carbohydrazide	
0·003144	2·2535	1·02028
0·001448	2·2263	1·01925
0·002432	2·2474	1·01990
	Symm. diphenyl carbazone	
0·005987	2·3207	1·02171
0·004370	2·2880	1·02081
0·003357	2·2645	1·02022
0·004937	2·2983	1·02107
	Symm. diphenyl thiocarbazone	
0·000412	2·2091	..
0·001261	2·2140	1·01925
0·001140	2·2137	1·01911

DISCUSSION

The moments of the derivatives of carbohydrazides can be interpreted by comparison with those of amides, ureas and hydrazides. The method of evaluation of the modification of bond moments due to induction along the polarizable bonds developed by Smith, Ree, Magee and Eyring[10] has been applied to amides like formamide and urea[9] and hydrazides like formhydrazide[8] and carbohydrazide. Table III contains values for the formal charges for each atom or group calculated by the above method for urea and carbohydrazide and Table IV the values of the calculated and observed moments.

TABLE II

	Symm. diphenyl carbohydrazide	Symm. diphenyl carbazone	Symm. diphenyl thiocarbazone
Hedestrand α ..	9·748	9·555	3·100
Hedestrand β ..	1·289	0·833	1·871
Molar refraction (cm.^{3})*	67·03	65·65	74·24
Total polarisation (cm.^{3})	352·09	356·52	200·26
Orientation polarisation (cm.^{3})	285·06	290·87	126·02
Dipole moment (D) ..	3·77	3·81	2·51

* Calculated from the bond refractions of Denbigh.

The tabulated charges assigned to various parts of the molecule is facilitated by reference to Figs. 1 A and B.

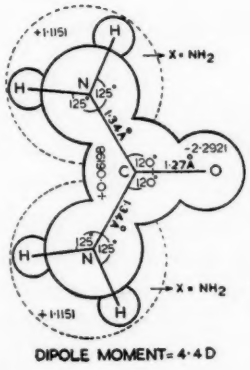


FIG. 1 A. Urea

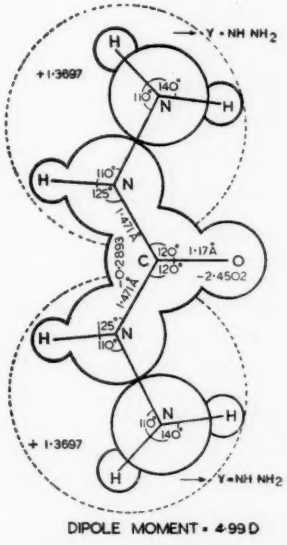


FIG. 1 B. Carbohydrazide

TABLE III

Atom or group	Urea	Carbohydrazide
1. C (carbonyl) ..	+ 0·06198	− 0·2893
2. X (amide or hydrazide)	+ 1·1151	+ 1·3697
3. O ..	− 2·0664	− 2·4502

TABLE IV

Dipole moment values in Debyes

Compound	Calculated by SRME method	Observed
Formhydrazide ..	2·3	2·24 (Dioxan)[8]
Acethydrazide ..		3·145 (Dioxan)[8]
Benzoic hydrazide ..		3·265 (Benzene)[3]*
Carbohydrazide ..	4·99	..
Diphenyl carbohydrazide		3·772 (Dioxan)
Diphenyl carbazone ..		3·800 (Dioxan)
Diphenyl thiocarbazone ..		2·500 (Dioxan)
Formamide ..	3·78[9]	3·37 (Benzene)[1]
		3·86 (Dioxan)
Acetamide ..	3·784	3·44 (Benzene)[1]
		3·90 (Dioxan)
Benzamide ..		3·65 (Benzene)[1]
		3·84 (Dioxan)
Urea ..	4·41	4·56 (Dioxan)[7]
Thiourea ..		4·89 (Dioxan)[7]
Diphenyl urea ..		4·60 (Dioxan)[6]
Diphenyl thiourea ..		4·85 (Dioxan)[6]

* Values recalculated using the modified Hedstrand method.

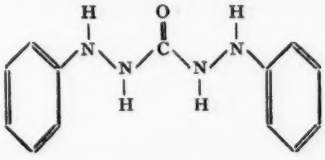
Since carbohydrazide is the hydrazine analog of urea, a comparison of the moments of acid hydrazides and carbohydrazides with amides and ureas as given in Table IV shows a striking similarity in the order of magnitude of the moments in the two cases. In the absence of measurements for carbohydrazide, the calculated value of 5 D for this compound indicates that the moment of the parent compound should be higher than that of the diphenyl compound. The mesomeric moment changes in the order formamide $-0{\cdot}56$ D, acetamide $-0{\cdot}344$ D, to urea $+0{\cdot}15$ D though such an indication could not be verified in the absence of measurements on carbohydrazide.

The case of symmetrical diphenyl carbohydrazide is interesting because it may have a lower moment than that of carbohydrazide due to the possible opposition of the moment from the main resonance in the parent compound and the ring resonance in the diphenyl derivative. If both forms are to contribute, the molecule must be coplanar.

(A)

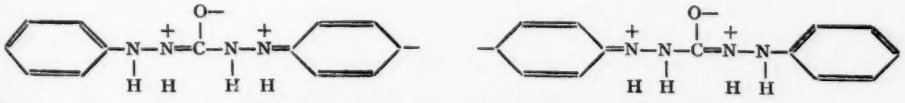
(B)

A study of the calotte models reveals that the coplanar form is possible only when the molecule is arranged with the phenyl groups,



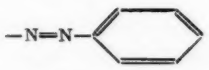
in which case the moment from the ring resonance would be in a direction which reduces the moment from the main resonance. Further more with a phenyl group on both end nitrogens a new resonance is possible between the following forms

(C)

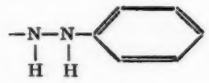


In the case of symmetrical diphenyl urea, the ring resonance reinforces the main resonance in the other part of the molecule due to conjugation and the negative charge can oscillate from one phenyl group to the other, the

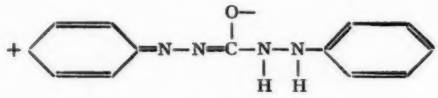
two nitrogens being positively and the oxygen negatively charged and the contribution of these equivalent structures will increase the moment. However, the two symmetrically placed phenyl groups thus introduce some factors which decrease the moment and others which increase it, so that there is little increase in the moment of diphenyl urea over that of the parent compound, whereas the moment of symmetrical carbohydrazide is lower than that of carbohydrazide due to the opposition of the two types of resonance. The fact that the observed moment of symmetrical diphenyl carbazone is almost the same as that of diphenyl carbazide, shows that the contribution of the moment of the



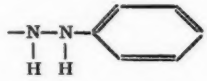
group to the resultant moment of the molecule is almost the same as that of the



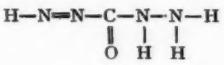
group. As in the case of diphenyl carbazide resonance of the type



operates in opposition to the ring resonance of the



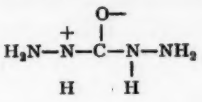
group so that the moment of diphenyl carbazone is almost the same as that of diphenyl carbazide. However, the moment of the parent compound



was not calculable by the Smith Ree Magee and Eyring method, due to difficulty of calculation of values of γ_{HN-N-C}. The value for diphenyl thiocarbazone is anamalous in that the value is much less than that expected.

The dipole moment values for the phenyl hydrazine derivatives of carbonic acid indicate clearly that these compounds do not exist as ' Zwitter ions', in which in addition to a separation of charge, a shift of a proton is necessary

to form it from the normal molecule. The Zwitterionic structure has been discarded in favour of the structure of the type



which also has a separation of charge but in which there is no shift of a proton for its formation. The normal melting points of the carbohydrazide derivatives support this conclusion. Thus the partial resonance structures postulated above can adequately account for their behaviour in dioxan.

Summary

Dipole moment measurements have been made for the following phenyl hydrazine derivatives of carbonic acid, namely diphenyl carbohydrazide, diphenyl carbazone and diphenyl thiocarbazone in dioxan solution. The values obtained are 3·77, 3·80 and 2·50 (all in Debye units) respectively. The structures of these compounds have been discussed with particular reference to resonance in these molecules.

Acknowledgment

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STUDIES IN OXIDATION: OXIDATION OF SOME ALIPHATIC SECONDARY ALCOHOLS WITH CHROMIUM (VI) OXIDE—PART I

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Introduction

The kinetics of the oxidation of isopropyl alcohol by Chromium (VI) oxide has been well investigated by Westheimer and his school[10–16] while Chatterji and Antony[2] have studied the oxidation of secondary butyl alcohol and secondary hexyl alcohol by the same oxidising agent. The oxidation was carried out in aqueous medium in the presence of perchloric acid at constant ionic strength. The reaction rate was found to be of the fourth order—first with respect to the acid chromate ion (which is taken to be the active oxidising species under the experimental conditions) and the alcohol, and second order with respect to the hydrogen ion under conditions of high acidity. At low acid concentrations the reaction was of the first order with respect to the hydrogen ion. More recently Roček[8] has questioned the Westheimer approach to the problem.

Earlier work has generally involved variations in pH and there is no satisfactory study of the influence of substituents or solvents. The accepted mechanism of Westheimer has not been proved unequivocally. The present communication reports the results of studies of a series of aliphatic secondary alcohols under controlled conditions.

Experimental

"Absolute" isopropyl alcohol was prepared by the method of Lebo.[4] The alcohol so obtained contained less than 0·1% of water, b.p. 82·4°. Butanol-2 was purified by refluxing first over freshly ignited calcium oxide and then with magnesium turnings (Jones and Christiansen),[3] b.p. 99·5°. Pentanol-2 and Octanol-2: The alcohols were kept for a few months over dry potassium carbonate and fractionally distilled (Pickard and Kenyon).[7] Acetic acid was purified by distillation with chromic acid by the method of Orton and Bradfield,[6] b.p. 117·7°. Pyridine: A.R. grade pyridine was purified by the procedure of Leis and Curran,[5] b.p. 115·8°. Chromic acid:

Merck extra pure variety chromium (VI) oxide was twice recrystallised from conductivity water and stock solutions were prepared in conductivity water. Potassium acetate: Merck pure quality potassium acetate was dehydrated and kept in a desiccator just before use.

Kinetic study.—The kinetic runs were made at four temperatures between 35° C. and 50° C. with an ionic strength of 0·4 the pH being maintained at 3·5 by an acetate buffer. Under these controlled conditions, the reaction was followed by iodometric titration of the unreacted chromic acid. Typical runs are presented in Table I. Plots of $\log_{10} (a - x)/(b - x)$ against t gave very good straight lines, indicating that the reaction is of the second order (Fig. 1).

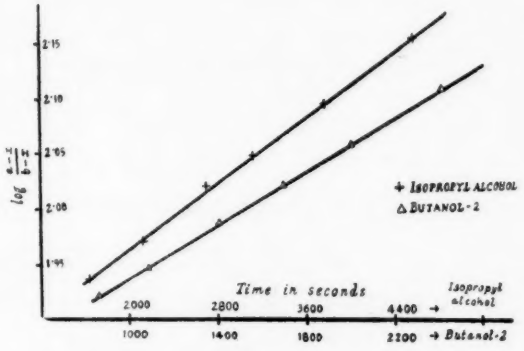

Fig. 1

Completion of the reaction.—10 c.c. of a solution of 1·5 molar in isopropyl alcohol, 0·1 M chromic acid was allowed to react in 70% aqueous acetic acid under the experimental conditions until the yellow colour due to the chromic acid disappeared completely. A 2 c.c. aliquot of this solution was pipetted into 50 c.c. of a 2 N HCl solution saturated at 0° C. with 2 : 4 dinitrophenylhydrazine; the acetone 2: 4 dinitrophenylhydrazone was obtained in 94 ± 2% yield of theoretical. The derivative, after one recrystallisation melted at 124–25° C. Similar yields were also obtained with the other alcohols.

The good constants for k_2 (Tables II–V) show that the reaction is of the second order in all cases under conditions of constant pH—first with respect to the gross concentration of hexavalent chromium and that of the alcohol—a result quite in accord with that of Westheimer and Cohen (*loc. cit.*, 1952). Although Westheimer has used the concentration of $HCrO_4^-$ in his rate

RESULTS AND DISCUSSION

TABLE I

Oxidation of (a) *Isopropyl alcohol,* (b) *Butanol-2,* (c) *Pentanol-2 and* (d) *Octanol-2 by chromic acid in 70% acetic acid at 50° C.*

	(*a*)	(*b*)	(*c*)	(*d*)
Concentration of alcohol	0·44305 M	0·4440 M	0·1666 M	0·1498 M
Concentration of chromic acid	0·006907 M	0·006797 M	0·00799 M	0·006832 M

(a) *Strength of thiosulphate* 0·009010 *N*

Time (sec.)	..	526	774	1205	1645	2124	2690	3116	3774	4570
Titre (m.l.)	..	10·4	10·05	9·4	8·5	7·85	6·95	6·55	5·85	5·1

(b) *Strength of thiosulphate* 0·01024 *N*

Time (sec.)	..	318	557	857	1094	1405	1698	2000	2418	2789
Titre (m.l.)	..	9·1	8·5	7·75	7·3	6·65	6·15	5·65	5·0	4·4

(c) *Strength of thiosulphate* 0·01115 *N*

Time (sec.)	..	1338	1866	2546	3149	4222	4939	5602	6922
Titre (m.l.)	..	9·1	8·4	7·75	7·2	6·15	5·6	5·3	4·4

(d) *Strength of thiosulphate* 0·01114 *N*

Time (sec.)	..	728	1360	1927	2513	3402	4270	6104	8593
Titre (m.l.)	..	8·5	7·9	7·5	6·8	6·4	6·0	4·9	3·9

equations, the use of gross concentration of hexavalent chromium is to be preferred under our conditions, for data regarding the equilibrium

$$Cr_2O_7^{--} + H_2O \rightleftharpoons 2\ HCrO_4^- \qquad (1)$$

are lacking in aqueous acetic acid solutions and consequently one is not certain of the particular species of hexavalent chromium that acts as the active oxidant. Further it is highly probable, as Westheimer himself has

TABLE II

Isopropyl alcohol

(Rates as $k_2 \times 10^5$ l.mole.$^{-1}$ sec.$^{-1}$ and $\mu = 0{\cdot}4$ in all cases)
Concentration of chromic acid: 0·00669 M.
Concentration of alcohol: 0·45145 M.

Temperature \ Percentage	30%	40%	50%	60%	70%
35° C.	0·6782	1·387	2·7136	5·832	13·58
40° C.	0·9822	1·985	3·9047	8·3532	19·03
45° C.	1·479	2·934	5·6654	11·610	26·686
50° C.	2·2034	4·6194	7·800	16·203	40·37

TABLE III

Butanol-2

Concentration of chromic acid: 0·006797 M.
Concentration of alcohol: 0·4442 M.

Temperature \ Percentage	30%	40%	50%	60%	70%
35° C. ..	1·2555	2·498	4·983	10·31	25·70
40° C. ..	1·7146	3·4494	7·152	14·45	34·67
45° C. ..	2·475	4·884	10·26	20·18	29·27
50° C. ..	3·548	6·394	13·62	26·67	64·91

observed (*loc. cit.*, 1952) that in systems of low dielectric constant, such as in acetic acid-water mixtures, the position of equilibrium in the system

$$HCrO_4^- + H_3O^+ \rightleftharpoons H_2CrO_4 + H_2O \qquad (2)$$

TABLE IV

Pentanol-2

Concentration of chromic acid: 0·00799 M.
Concentration of alcohol: 0·1669 M.

Temperature \ Percentage	30%	40%	50%	60%	70%
35° C. ..	1·724	3·324	6·791	14·97	30·04
40° C. ..	2·317	4·786	9·348	18·70	42·58
45° C. ..	3·562	6·877	13·84	27·07	57·90
50° C. ..	4·698	9·469	18·81	35·67	77·79

TABLE V

Octanol-2

Concentration of chromic acid: 0·006837 M.
Concentration of alcohol: 0·14975 M.

Temperature \ Percentage	60%	70%	80%
35° C. ..	11·89	28·18	77·62
40° C. ..	16·60	38·02	99·91
45° C. ..	24·96	53·31	140·3
50° C. ..	31·59	69·84	190·5

would lie more to the right. This is well brought out by the constancy of the rate constants. It has also been observed that in the concentration range employed (0·006 M) little deviation occurs irrespective of the gross concentration of chromium (VI) or that of the $HCrO_4^-$ being used, imperfections entering only with higher concentrations of chromic acid due to pronounced changes in the equilibrium system (1).[10]

TEMPERATURE DEPENDENCE OF THE RATE OF OXIDATION

The temperature dependence was determined for each solvent composition for all the four alcohols. The results were plotted as log k_2 against 1/T or as log K_2/T against 1/T.[1] The values derived for the thermodynamic constants for the series are given below (Table VI).

TABLE VI

Solvent: 70% *acetic acid*

Alcohol	$E_{\blacktriangle}$ (cal./mole)	log PZ	$\Delta S\pm$
Propanol-2 ..	12860	5·2595	−34·57
Butanol-2 ..	12210	5·0660	−35·5
Pentanol-2 ..	11890	4·9192	−36·14
Octanol-2 ..	12280	5·1678	−35·03

A remarkable feature of the reactions is the strict linearity observed in the log k_2-1/T curves (Fig. 2) for all the solvent compositions and it is interesting to recall here the objections raised by Svirbely and Warner[9] against the conventional method of evaluating activation energies in reactions that are affected by the dielectric constant of the solvent. The observed behaviour proves that there is no change in the energy of activation within the temperature range studied and that the correction factor in the expression for iso-dielectric activation energy

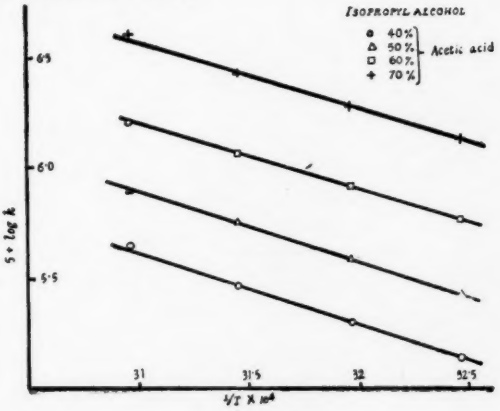

FIG. 2

$$E_D = E_{app} + R\left(\frac{\delta lnk}{\delta D}\right)_T \frac{dD}{d(1/T)}$$

is small in comparison with E_{app} (apparent, *i.e.*, experimental activation energy).

The reaction rate is slowest in 30% acetic acid and increases with increasing proportions of acetic acid. This effect of solvent on the course of the reaction and the import of the various thermodynamic constants will be considered in a later communication.

Effect of products on the rate of the reaction.—The rates of oxidation were studied in the presence of various small amounts of both the inorganic and organic products (Table VII). It is seen that the organic product, *viz.*, the corresponding ketone has no effect on the oxidation while the inorganic product, *i.e.*, chromium acetate inhibits the reaction rate.

TABLE VII

Alcohol	Chromium acetate	Acetone (OR) methyl-ethyl ketone	$k_2 \times 10^5$	$k_2 \times 10^5$ (in absence of products)
Isopropyl alcohol ..	0·004304 M	..	11·88	13·58
	0·007505 M	..	11·77	
	..	0·1330 M	13·52	
Butanol-2 ..	0·007515 M	..	30·67	34·67
	..	0·1123 M	34·42	

The constants are for oxidation in 70% acetic acid at 35° C. for isopropyl alcohol and at 40° C. for butanol-2.

The essential features of the Westheimer mechanism for the chromic acid oxidation of isopropyl alcohol in aqueous solutions are the preformation, by a rapid reversible reaction, of the ester, monoisopropyl chromate, which then decomposes in a slow, rate-determining step involving a base (*e.g.*, water) to acetone and a chromium (IV) compound. The secondary hydrogen atom is believed to be lost as a proton in the rate-determining step, bases like pyridine catalysing this oxidation.[16]

$$H^+ + HCrO_4^- \underset{\longrightarrow}{\overset{\text{Fast}}{\longleftarrow}} H_2CrO_4 \qquad (3)$$

$$(CH_3)_2\,CHOH + H_2CrO_4 \underset{\longleftarrow}{\overset{\text{Fast}}{\longrightarrow}} (CH_3)_2CH{-}O{-}CrO_3H + H_2O \qquad (4)$$

$$(CH_3)_2C\begin{matrix}H\\ \diagup\\ \diagdown\\ OCrO_3H\end{matrix} + H_2O \xrightarrow{\text{Slow}} (CH_3)_2CO + H_3O^+ + HCr^{IV}O_3^- \qquad (5)$$

At the time when it was put forward, the ester mechanism did, indeed, satisfactorily account for the majority of the facts known about the oxidation of secondary alcohols. One of the facts accounted for in this way was the effect of acetic acid on the rate of oxidation of isopropyl alcohol. The large increase in rate in 85% acetic acid was interpreted by Westheimer on the assumption that acetic acid displaced the esterification equilibrium[4] in favour of the ester. But the retardation in rate exhibited with increasing proportions of water goes against the proton-abstraction theory. It was believed that water could function as a base in the rate-determining step facilitating the removal of a proton from the field of action. The results of the present study, as indeed those of others in the field,[17] show that the rate of oxidation decreases with increasing proportions of water. Thus it is seen that the most likely base, water, if anything, inhibits the reaction even under conditions of constant hydrogen-ion concentration.

Further, the effect of Pyridine on the rate was studied to clarify the base-catalysis. The results are given in the Table VIII.

TABLE VIII

Effect of added pyridine on the rate of oxidation

Concentration of isopropyl alcohol: 0·4 M. Temperature: 50° C.
Concentration of chromic acid: 0·006735 M. Solvent: 70% Acetic acid.
In the absence of added pyridine: $k_2 \times 10^5$: 40·37.

Concentration of pyridine	.. 0·006885 M	0·017665 M	0·03203 M
$k_2 \times 10^5$	.. 40·09	38·86	33·59

Catalysis of the oxidation, which has been quoted as important experimental support for Westheimer's mechanism, could not be confirmed,

Curiously enough, using several different concentrations of pyridine no acceleration of the reaction could be obsserved. A slight retardation is actually noticeable (*cf.* Roček and Krupička, *loc. cit.*).

In the series of aliphatic alcohols investigated, it is seen that the rate of oxidation increases in the order Pentanol-2 > octanol-2 > butanol-2 > propanol-2.

In the series of aliphatic alcohols investigated it is seen that the rate of oxidation increases in the order pentanol-2 (57·903) > octanol-2 (53·306) > butanol-2 (49·27) > propanol-2 (26·69). The values in brackets represent the second order constants, at 45° in 70% acetic acid, multiplied by 10^5.

Considering that all these alcohols differ only with reference to one of the alkyl groups attached to the secondary carbon atom (the other being a fixed methyl group) it is surprising that the rates of oxidation observed experimentally run counter to the Westheimer hypothesis. If one were to imagine the operation of only the inductive effect due to the substituent alkyl groups, the ease of proton loss in the rate-determining step, in the series of alcohols studied should be the reverse of the experimental findings.

The slight reversal in the rate between pentanol-2 and octanol-2 which might look anomalous at first sight, might actually be due to the falling off of the inductive effect with the chain length of the alkyl group or partly due to the steric effect operating, or both.

It is thus clear that the mechanism for the oxidation of alcohols is still not settled. A detailed mechanism for the oxidation with further experimental results will be communicated later.

SUMMARY

The oxidation of isopropyl alcohol, butanol-2, pentanol-2 and octanol-2 by chromium (VI) oxide, has been studied in acetic acid-water mixtures under conditions of constant ionic strength and hydrogen-ion concentrations, between 35° C. and 50° C. The reaction is of the second order and the rate increases with increasing proportions of acetic acid. The results of the present study are not easily explicable on the basis of the hitherto generally accepted mechanism of Westheimer.

ACKNOWLEDGEMENT

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CONTENTS

PAGE

Huyghens' Principle and the Diffraction of Light. Part I. Theoretical Considerations . . . . . Sir C. V. Raman 83

A Note on the Interaction between Nucleon and Anti-Nucleon . . . . . Alladi Ramakrishnan, N. R. Ranganathan and S. K. Srinivasan 91

Theory of the Anomalous Dispersion Method of Determining the Structure and Absolute Configuration of Non-Centrosymmetric Crystals . S. Raman 97

The Microwave Spectrum of Methyl Cyanide and *l*-Type Doubling in CH_3CN, CH_3NC, CH_3CCH and CF_3CCH . . . . . T. S. Jaseja 103

The Photolytic Separation of Uranium from Aluminium and Thorium, Cerium and Lanthanum . . . . . K. Singh, Balaram Sahoo and D. Patnaik 123

The Problem of the Composition and Structure of Potassium Cyanocobaltate (II) . . . . . K. M. Abubacker and Wahid U. Malik 132

A General Transform—Gauss Transform . . . . . A. K. Rajagopal 140

The Dipole Moments and Molecular Structure of Phenylhydrazine Derivatives of Carbonic Acid . . B. S. Subba Rao and Sundaresa Soundararajan 146

Studies in Oxidation: Oxidation of Some Aliphatic Secondary Alcohols with Chromium (VI) Oxide—Part I . . . . . N. Venkatasubramanian 156